NASA CR 51374

A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

Annual Summary Report and
Annual Materials Report for the Period
February 4, 1961 to February 3, 1962

To

N63 21735

GEORGE C. MARSHALL SPACE FLIGHT CENTER
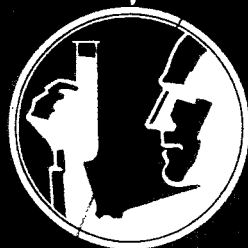NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Huntsville, Alabama

SOUTHERN RESEARCH INSTITUTE

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GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Huntsville, Alabama

Project 1259, Report 13

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Contract NAS 8-1510

Southern Research Institute
Birmingham, Alabama
February 28, 1962
5171-1259-XIII

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ABSTRACT

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Compounds containing silicon-nitrogen bonds have been studied in a search for materials that may be useful in space vehicles. There are at least two potentially valuable unique properties that are found in some silicon-nitrogen compounds. These features are good adhesion to metals and ceramics and the ability to undergo conversion to thermosetting polymers of extraordinary thermal and chemical stability. In addition to the advantages some silicon-nitrogen compounds possess, they are equal and possibly superior to the siloxanes in thermal stability and versatility of physical states. The sensitivity of silicon-nitrogen compounds to moisture varies over a wide range from extreme susceptibility to extreme inertness.

The outstanding types of silicon-nitrogen compounds regarding possible uses in space vehicles are the following:

Silazanes made by the moderate-temperature reactions of silicon halides with ammonia and amines.

Thermoplastic silylamine polymers made by amine exchange reactions between silazanes and organic diamines, and also by heating some silazanes to 350-450°C.

Elastomers made by curing the polymer made from dimethyldichlorosilane and ethylenediamine.

Thermosetting silylamine polymers made by heating some silazanes in the range of 450-550°C.

Polymers made from hydrazine and chlorosilanes.

Compounds and polymers made from silicon tetrachloride and methylamine.

Compounds and polymers made from silicon oxychlorides and ammonia or amines.

Compounds made from silazanes and silicon tetrafluoride.

At present the most promising high-temperature applications for silicon-nitrogen compounds and polymers appear to be coatings, hydraulic fluids, and impregnating resins for gaskets.

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A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

I. PURPOSE AND CURRENT STATUS OF THE PROJECT

The purpose of this project was to investigate compounds and polymers that contain silicon-nitrogen bonds to determine whether they may be useful in space vehicles. The planned research included studies of different types of syntheses of silicon-nitrogen polymers, the structures of the polymers, and the development of useful applications of the materials. New materials were regarded as potentially valuable if they had a high degree of stability toward heat, water, air, or liquid oxygen, and if they had physical properties that were appropriate for lubricants, sealants, adhesives, elastomers, or structural plastics.

This investigation has been in progress for two years. The first year's research was summarized in a report dated February 20, 1961.[1] The present report summarizes the second year's research, and the current status of the investigation is as follows.

From the screening of different types of silicon-nitrogen compounds, the outstanding types are silazanes, polymeric silylamines made from ethylenediamine, silylhydrazine polymers, polymeric silylamines made from silicon tetrachloride and methylamine, silylamines made from silicon oxychlorides, and addition compounds made from silazanes and silicon tetrafluoride.

The properties of the silicon-nitrogen compounds are most easily summarized in three different groups. The first is silazanes and silylamines that have not been exposed to high temperatures. Many of them are liquids or crystals. They are greases if they are polymers of low molecular weight, and they are wax-like solids if they have molecular weights of several thousand. Most of them are easily hydrolyzed by water, although some, such as hexaphenylcyclotrisilazane, are protected by steric factors and are not completely destroyed by boiling water in 30 minutes. Some have good thermal stability—for example, nonamethylcyclotrisilazane was changed almost imperceptibly by heating at 400°C for 19 days in an evacuated sealed tube. Some of these compounds, or mixtures of them, merit consideration as hydraulic fluids.

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1. Report 14, Contract DA-01-009-506-ORD-829, ID No. 0602-00-60, February 20, 1961.

The second group includes silazanes and silylamines that have been heated in the range of 450-550°C. At that temperature, condensation polymerization occurs, and brittle inert solids are formed. Many of these polymers are potentially valuable as coatings, and all that have been examined are hydrolytically stable.

The third group is the silylamine polymers made from ethylene-diamine. These polymers are converted to elastomers by heating in air at 350-400°C. They have very little strength, but they are interesting as coatings and gasket impregnants. The curing process converts them almost entirely to siloxanes, but they appear to have some advantages in terms of adhesion, endurance, and flexibility at high and low temperatures. When mixed with other silazanes and made into coatings for metals or ceramics they impart flexibility to the cured products but decrease thermal stability.

II. STUDY OF DIFFERENT TYPES OF SILICON-NITROGEN COMPOUNDS

Ten different types of silicon-nitrogen compounds were studied as part of the screening program to determine which types of silicon-nitrogen compounds have desirable characteristics. These ten were in addition to the silazanes that have been studied continuously.[1] The silazanes are evidently the most versatile group of silicon-nitrogen compounds.

A. Silylhydrazine Polymers

1. Discussion

Hydrazine, being a polyfunctional molecule, offers the possibility of polymerization with a dichlorosilane. Wannagat and Liehr[2] reported the preparation of a polymer with a molecular weight of 3500 by adding hydrazine to dimethyldichlorosilane. Their polymer was glassy, colorless, and benzene-soluble.

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2. U. Wannagat and W. Liehr, Angew. Chem. **69**, 783 (1957).

In one attempt to follow the procedure of Wannagat and Liehr, adding hydrazine to the silane, we obtained a polymer that was a viscous cloudy white oil. In a second attempt, adding the silane to hydrazine, we obtained a polymer that was a cloudy white grease. The molecular weight of the second polymer was estimated by vapor osmometry to be approximately 1100. Its elemental composition is given in Table I. Evidently the degree of polymerization of both polymers was lower than that achieved by Wannagat.

When attempts were made to form coatings on metals by curing thin films on metal panels at temperatures up to 550°C, clear colorless films were obtained. They were rather brittle but had high thermal stability. As noted with some of the phenyl silazanes, the aluminum substrate was melted by rapid heating while the film remained intact.

To determine whether further polymerization would occur on heating, the silylhydrazine polymer with a molecular weight of 1100 was heated for two hours at 175-520°C. Some gas was evolved, while the polymer gradually changed from colorless to amber to brown as heating progressed. The final product was a liquid while hot, but after cooling it was a hard brown solid, soluble in benzene, and containing 14.4% nitrogen. The silylhydrazine polymer evidently does not undergo conversion to a thermosetting polymer as readily as the phenylsilazanes do.

In another experiment, films of the silylhydrazine polymer were compared on aluminum panels with films of the hexaphenylcyclotrisilazane polymer. Both films were applied in benzene solutions and cured at 215°C and at 550°C. Subsequently both films were heated at 600°C for one hour. Both crazed badly but remained attached to the panels. The hexaphenyl film turned brown, but the hydrazine film remained colorless. Both films appeared to protect the aluminum from attack by acid and alkali.

2. Experimental Details

The first reaction was run by the method of Wannagat and Liehr.[2] Hydrazine was dried by fractional crystallization until the melting point was 1-2°C. In a 300-ml, 3-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 125 ml of benzene and 21.55 g (0.167 mole) of dimethyldichlorosilane. The flask was swept with nitrogen, and 16.0 g (0.5 mole) of hydrazine was added dropwise with stirring over a period of 20 minutes. The temperature was kept below 50°C. After addition was complete, the mixture was stirred and refluxed for two hours. Because the Beilstein test was positive for halogen in the supernatant liquid, another 1.0 g (0.03 mole) of hydrazine was added, and refluxing was resumed for 30 minutes. Then the Beilstein test was negative. The mixture was filtered, and the benzene was removed from the clear organic liquid by distillation. The final still pot conditions were 150°C at 3 mm pressure. The residue weighed 13.5 g, 92% of the theoretical yield (14.5 g) considering $Si(CH_3)_2(NH)_2$ to be the formula. If the end groups are considered, the expected ratio of hydrazine to silicon is higher than 1:1, and consequently the expected yield is higher.

The product was a white cloudy viscous liquid. The molecular weight was estimated cryoscopically in benzene to be 616. When heated on a spatula, the product bubbled, smoked, and finally solidified to a film where it was thin. Where it was thick, bubbles formed which were flexible. After the spatula was heated until it was dull red, the bubbles were brittle, but they did not darken.

The silylhydrazine polymer was heated in a test tube while it was being flushed with nitrogen. Gentle boiling began at 170°C, and the temperature was gradually increased to 480°C in 14 minutes. A sample taken at that time cooled to a colorless heavy grease. Two minutes later the temperature was 530°C. Throughout the range of 480-530°C bubbling was rapid and most of the product apparently had distilled when 530°C was reached. The remaining material then started to solidify to a foamed powder with some discoloration. However, the tube had become red hot during solidification.

The second synthesis was made in the same manner as the first except that the order of addition was reversed. Hydrazine, 16.0 g (0.5 mole), was dispersed by stirring in 125 ml of benzene. Dimethyldichlorosilane, 21.55 g (0.167 mole), was added with stirring over a period of 20 minutes. When the addition of the silane was complete, the Beilstein test was negative. The mixture was refluxed for two hours, filtered, and distilled as before. The residue weighed 13.6 g. It was a white translucent heavy grease. The molecular weight was estimated cryoscopically to be 575. However, confidence in the cryoscopic method was low, and so the molecular weight was checked by vapor osmometry. The molecular weights by vapor osmometry in benzene were 1200, 995, and 1080; the molecular weights in carbon tetrachloride were 1010 and 1010. The average of the five results was 1060. The elemental analysis of this silylhydrazine polymer is listed in Table I.

A prolonged heating experiment was made to determine whether the second silylhydrazine polymer would undergo the condensation polymerization that is common for the phenylsilazanes. The polymer, 2.2 g, was placed in a test tube that had a side arm. The tube was flushed with nitrogen and nitrogen was passed slowly into the side arm throughout the reaction. After heating with a gas burner for one minute, the temperature reached 175°C and bubbles began to appear. Heating was continued, and the temperature reached 240°C in 12 minutes, 340°C in 37 minutes, 440°C in 82 minutes, 510°C in 112 minutes, and 520°C in 114 minutes. Foaming occurred throughout the entire period. The temperature was held at 520°C for five minutes and then the liquid was cooled. It became a hard brown solid and weighed 1.1 g. Its nitrogen content was 14.43%, as shown in Table I. The temperature would have been carried higher if more polymer had been present. Although the condensation to a thermosetting polymer was not observed, it might yet occur at a higher temperature.

Films made from hexaphenylcyclotrisilazane and silylhydrazine, the second polymer, were compared while they were being cured and subsequently at 600°C. The polymers were spread on aluminum plates from 15% solutions in benzene. The benzene was evaporated with nitrogen, and the films were cured in nitrogen for 15 minutes at 215°C. The hydrazine film smoked and remained soft while the hexaphenyl film became hard. The films were then heated in air at 550°C for five minutes. Both films stopped smoking in this time, and both were smooth and clear. The hydrazine film was colorless, and the hexaphenyl film was yellow. Both were heated at 600°C for one hour in air. Both films were severely crazed at this time, but both were still attached to the aluminum. The hydrazine film was colorless, and the hexaphenyl film was brown. Hydrochloric acid, 20%, and sodium hydroxide, 8%, caused rapid evolution of hydrogen at the cracks in both films but appeared to leave the films undamaged.

Table I. Data on the Silyhydrazine Polymer

	Polymer as first prepared[a]	Polymer after heating[b]	Theoretical for	
			$(C_2H_8N_2Si)_x$ [c]	$(C_6H_{20}N_4Si_3)_x$ [d]
Carbon, %	32.60		27.24	30.99
Hydrogen, %	8.32		9.14	8.67
Nitrogen, %	17.50	14.43	31.77	24.10
Silicon, %	34.6		31.85	36.24
Total, %	93.02			
Molecular weight (vapor osmometry)	approximately 1100			

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[a] Made by adding dimethyldichlorosilane to hydrazine in benzene (the second polymer).

[b] Polymer refluxed for two hours. The final temperature was 520°C and the cooled product was a brown solid.

[c]
```
    Me  H   H
     |
-   Si - N - N -
     |
    Me
```

[d]
```
               Me₂  H
        H     /Si - N
             /       |
 - N - N ⟨          |
             \ Si - N - Si -
               Me₂        Me₂
```
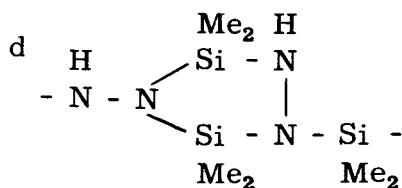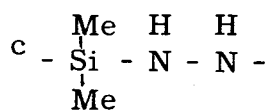
B. <u>Reaction of Silicon Tetrachloride with Methylamine and Ethylenediamine</u>

1. Discussion

Silicon tetrachloride was treated with methylamine to produce a crystalline, benzene-soluble, silicon-nitrogen compound that was sensitive to heat and moisture. The crystalline compound was converted by heating to an infusible, insoluble, wax-like solid of high thermal and chemical stability. The characterization of the two products is incomplete, but the information obtained suggests that they will be interesting theoretically and practically.

Previous work with silicon tetrachloride and ammonia had been disappointing, because the products were intractable white powders that were extremely sensitive to moisture.[1] In contrast, the reaction of silicon tetrachloride with methylamine produced a soluble crystalline solid that could be polymerized to a stable solid. The polymerization that occurs on heating is probably a result of the elimination of methylamine between $\equiv$ Si - $NHCH_3$ groups to form $\equiv$ Si - NCH_3 - Si $\equiv$ groups.

Two interesting opportunities are presented by the tetraaminosilane polymers. One is based on Fessenden's conviction[3] that a high nitrogen/silicon ratio is important to thermal stability. The other is the possibility of the use of the tetraaminosilanes in syntheses such as copolymerization and amine exchange.

Attempts to produce coatings from the tetraaminosilane polymer were inconclusive. Polymerization on the surface of glass and metals did occur, but the resulting coating was evidently discontinuous and friable. However, it showed some adhesion which suggests that the tetraaminosilane may be useful as a coating for glass fibers used in reinforced plastics.

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3. R. Fessenden, private communication, letter of July 25, 1961, to NASA (Dr. W. R. Lucas).

In the first reaction of silicon tetrachloride with methylamine, no attempt was made to keep the temperature low; and when the last traces of solvent were removed at 220°C and 3 mm pressure, the product solidified. Thereafter it was infusible and insoluble. In the second reaction the benzene was removed at reduced pressure, and the temperature was kept below 70°C. Impure crystals, melting at 104-107°C, were obtained. The elemental analysis, Table II, indicated 9% oxygen, which discouraged any deductions about structure. The nitrogen content was 31.3%. In the third reaction, extra effort was made to keep the temperature low and to purify the starting materials. The recrystallized product melted at 116-121°C and had approximately the correct analysis for a compound with a nitrogen-silicon ratio of 3:1. A cyclic silazane structure is possible, as shown in Table III. However, the analysis, especially the carbon content, does not adequately confirm these suppositions. The compound will have to be purified further before its structure can be deduced.

As a continuation of the study of the compounds made from silicon tetrachloride, a reaction was run with ethylenediamine and silicon tetrachloride. The reactants were mixed in benzene with stirring. A mass of insoluble matter formed that was evidently a mixture of ethylenediamine hydrochloride and the silylamine reaction product. No soluble product could be obtained. Because of these discouraging results, no additional time was spent on the product.

2. Experimental details

The first reaction between silicon tetrachloride and methylamine was conducted as follows. In a 2-liter, 3-necked flask fitted with a stirrer, gas inlet tube, reflux condenser, and thermometer were placed 42.5 g (0.25 mole) of silicon tetrachloride and 1000 ml of benzene. Methylamine was passed over the surface of the stirred solution for 80 minutes and the temperature was kept below 30°C with an ice bath. Then the temperature was raised to 50°C, and methylamine was passed in for 90 minutes longer. After being stirred for an hour, the mixture stood overnight. The clear benzene layer was negative to the Beilstein test. After being refluxed for three hours, the mixture was filtered. The amine hydrochloride obtained was 68.5 g (67.5 g, theoretical). The benzene was removed by distillation in a 1.2 x 30-cm column. The final traces of benzene were removed at 150 mm pressure. As soon as the benzene had been removed, the pressure

Table II.   Physical Data and Elemental Analyses of the First Two Compounds Made from Silicon Tetrachloride and Methylamine

Analysis	Found				Theoretical	
	Sample 1 [a]	Sample 2 [b]	Sample 3 [c]	Sample 4 [d]	$C_2H_6N_2Si$ [e]	$C_4H_{16}N_4Si$ [f]
Carbon, %	25.87	28.15	26.43	26.73	27.87	32.40
Hydrogen, %	7.33	7.55	6.99	7.59	7.02	10.88
Nitrogen, %	26.74	31.30	29.73	25.32	32.51	37.78
Silicon, %	22.00	23.90	26.80	28.20	32.60	18.94
Remainder, % (presumably oxygen)	18.06	9.10	10.05	12.16	0	0
Neutral equivalent	42.60				43.09	37.07
Melting point,		104-107				

a First preparation.

b Second preparation, crystalline product as obtained without heating.

c Second preparation, heated one hour at 450°C.

d Second preparation, heated over a burner until evolution of gas ceased.

e $C_2H_6N_2Si$ $CH_3 - N - Si - N - CH_3$

f $C_4H_{16}N_4Si$ $CH_3NH - Si - NHCH_3$ (with $HNCH_3$ groups)
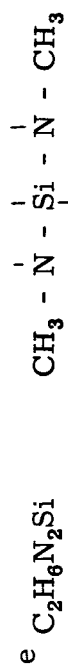
Table III. Elemental Analysis of the Third Compound (m.p. 116-121°C) Made from Silicon Tetrachloride and Methylamine

	Found		Elemental formula[a]	$C_4H_{16}N_4Si$[b]	Theoretical for $(C_3H_{11}N_3Si)_3$[c]	$C_2H_6N_2Si$[d]
Carbon, %	34.34	33.16	3.43	32.40	30.73	27.87
Avg.	33.75					
Hydrogen, %	9.89	9.50	11.60	10.88	9.46	7.02
Avg.	9.70					
Nitrogen, %	35.01	36.16	3.10	37.78	35.85	32.51
Avg.	35.59					
Silicon, %	22.9	23.3	1.00	18.94	23.96	32.60
Avg.	23.1					
Total, avg.	102.14					
Molecular weight (cryoscopic in benzene)	370				351.7	

a Elemental formula relative to Si = 1.

b Si(NHMe)$_4$

c

Me-NH—Si—HN-Me
    | NMe
MeN—Si—N—Si—NHMe
MeNH | NHMe
      Me
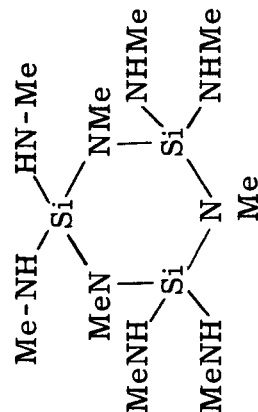
d MeN-Si-NMe

was reduced to 3 mm, and the pot temperature was increased. When the pot reached 220°C, there was no evidence of incipient distillation and the product had become very viscous. Accordingly, the distillation was discontinued, and nitrogen was admitted to the system. Later the product was solid, and it could not be remelted. It weighed 12.3 g. For purposes of calculating theoretical yield, two formulas were assumed representing

the extreme possibilities. One was $(CH_3N - \overset{|}{\underset{|}{Si}} - NCH_3)_x$, and the other

was $(CH_3NH)_4Si$. The most likely formula is between these two. Based on the first formula, the yield was 62% of the theoretical and based on the second it was 36%. Undoubtedly, some low-boiling silicon compound was lost during the distillation.

The solid product from silicon tetrachloride and methylamine contained 26.74% nitrogen. The theoretical value based on the first formula above is 32.51% and on the second is 37.78%. There was evidently some oxygen present.

The foamed solid product from silicon tetrachloride and methylamine did not dissolve in the common organic solvents, and it was only whitened slightly when boiled in 6N hydrochloric acid. However, no prolonged attempts were made to dissolve the compound. The thermal stability was estimated by heating in an evacuated sealed glass tube at 450°C for 1.5 hours. There was no visible change, and the gas evolved was 0.12 ml per gram. This figure places the solid product among the most stable compounds we have made. For comparative data see Reference 1.

The second reaction was conducted as follows. In a 2-liter, 3-necked flask fitted with a stirrer, gas inlet tube, reflux condenser, and thermometer were placed 42.5 g (0.25 mole) of silicon tetrachloride and 1000 ml of benzene. Methylamine was passed over the surface of the stirred solution for 80 minutes, and the temperature was kept below 30°C with an ice bath. Then the temperature was raised to 50°C and methylamine was passed in for 90 minutes longer. After being stirred for an hour, the mixture stood overnight. The clear benzene layer gave a negative Beilstein test. After being refluxed for three hours, the mixture was filtered. The amine hydrochloride removed was 67.1 g (67.5 g, theoretical).

The benzene was distilled through a Claisen still head until the pot temperature reached 85°C. At this point the liquid was about 50% benzene, and it was faintly cloudy. However, the cloudiness settled on cooling, and a clear solution remained. Several samples were taken to study their properties. When a few drops were spread on an aluminum plate in air, the benzene evaporated. First, a gelatinous mass appeared, and then the residue became crystalline. A few drops of the product were evaporated on a glass plate in an atmosphere of nitrogen, and then the remaining crystals were exposed to air. After 2.5 hours the carbon and hydrogen contents were down to 6.40% and 4.01% respectively, but microscopic examination revealed that the product was mostly or entirely crystalline. These crystals did not change visibly when heated on a spatula to red heat.

The benzene remaining in the main part of the product was removed at reduced pressure while the temperature was raised gradually to 70°C. The final pressure at 70°C was 2.5 mm. As the last of the benzene was removed, the mass crystallized. Even though care was taken to exclude moisture, some methylamine was distilled with the benzene. It is possible that condensation polymerization occurred between end-amino groups even at that low temperature, and so the methylamine may have been produced either by condensation of end-amino groups or by inadvertent admission of moisture.

A 2.0-g sample of the crystalline reaction product was heated in a flask with a narrow opening in an oven at 450°C for an hour. A large amount of smoke was evolved, and the product became solid in about 15 minutes. Heating was continued for 45 minutes longer, and during this time no further visible change occurred. The elemental analysis of the residue, which was 60% of the original, is given in Table II (Sample 3). A second controlled decomposition was done in a distilling flask over a burner. By this method gentle heat was applied at first. The residue was 85% of the original, and again it was a foamed solid with the analysis shown in Table II (Sample 4).

A third reaction was run between silicon tetrachloride and methylamine. Extra effort was made to keep the temperature low and to use pure starting materials. In a 1-liter, 3-necked flask fitted with a condenser, stirrer, gas-inlet tube, and thermometer were placed 500 ml of benzene and 42.8 g (0.25 mole) of recently distilled silicon tetrachloride. Methylamine was passed over the surface of the rapidly stirred liquid while the temperature was kept below 30°C. After 1.75 hours the temperature was allowed to rise to 55°C, and stirring was continued for 30 minutes at 55°C. There being no evidence of absorption of methylamine, as indicated by an inflated balloon attached to the condenser, the mixture was then refluxed for three hours. The Beilstein test for halogens in the supernatant liquid was negative. The mixture was centrifuged to remove amine hydrochloride. Another Beilstein test revealed some halogen, and consequently methylamine was passed in again for 1.5 hours in the same apparatus. The mixture was heated with stirring at 60-70°C for one hour with a positive pressure of methylamine, and then it was heated and stirred for one hour at atmospheric pressure. On standing, the insoluble matter settled. The clear liquid was pipetted off, and the benzene was removed by evaporation in a stream of nitrogen at 50°C. When most of the benzene had been removed, the mass crystallized. It was recrystallized very carefully from Skellysolve "B", the temperature ranges being 0° to 30°C. After four recrystallizations, the melting point of the crystals was 116-121°C. These were obviously impure, but it seemed preferable to learn more about the compound before going further. The elemental analysis is listed in Table III with several theoretical compositions for comparison. The analysis suggests a 3:1 ratio of N:Si. The molecular weight, as determined cryoscopically in benzene, was 370. This suggests that the compound is the cyclic trimer, pictured on Table III, but the data are not close enough to the theoretical values to consider the structure proven.

The reaction between ethylenediamine and silicon tetrachloride was run as follows: In a 1-liter, 3-necked flask fitted with a thermometer, stirrer, and dropping funnel was placed a solution of 60.1 g (1.0 mole) of dry ethylenediamine in 250 ml of benzene. Silicon tetrachloride, 42.5 g (0.25 mole), was added dropwise over 45 minutes while the mixture was being stirred rapidly. The temperature rose to 78°C. The reaction mixture was cloudy during the first half of the addition, and then a yellow lump formed on the stirrer. The lump broke up within a few minutes into

small lumps that did not disperse. The mixture was refluxed for three hours and the mixture was allowed to stand over a weekend. Ethylenediamine, 30. 1 g (0. 5 mole), was added, and stirring was resumed with refluxing, which was continued for four hours. At this point the product had the consistency of putty. On cooling it became hard. The clear supernatant liquid was negative to the Beilstein test. Usually, in reactions of this type, the silicon-nitrogen product is dissolved in the solvent, and the insoluble amine hydrochloride is removed by filtration. In this case filtration was not necessary. The liquid portion was separated from the insoluble matter by decantation, but distillation of it yielded no product. Prolonged extraction of the solid with xylene in a Soxhlet extractor failed to separate the silicon-nitrogen polymer from the amine hydrochloride.

C. Polymerization Through a Vinyl Group—Bis-(dimethylamino)-methylvinylsilane

1. Discussion

A silylamine with a vinyl group was desired to determine whether a useful silylamine polymer could be formed by polymerization of the vinyl groups. Bis-(dimethylamino)methylvinylsilane was prepared, and some polymerization of it was accomplished with peroxides, sodium, an azonitrile, and ultraviolet light; and the products were viscous liquids. Gamma radiation was not effective. The viscous liquid polymer from catalyzed polymerization hardened to a film when exposed to air. The highest molecular weight measured was 570.

In air, polymerization occurred simultaneously with the elimination of most of the nitrogen; and a clear, colorless, resilient polymer of low strength was produced. This clear rubbery polymer appeared to be thermally stable at 300°C, but it darkened slowly at higher temperatures. Its strength was somewhat greater than that of the cured ethylenediamine silazanes, but it was much less than that of ordinary rubber.

Vinylsilanes are evidently not easily polymerized.[4] Vinyl-trimethylsilane gave polymers of low molecular weight on prolonged heating at 155°C[5] in a sealed tube. Rochow[6] polymerized vinylsilane with ultraviolet light, but he obtained very small amounts of polymers. Mixer and Bailey[7] apparently are the only ones who have obtained fairly high molecular weights from vinyl silicon compounds. They made liquid polymers having molecular weights of **3,000-8,000** by heating vinyltri-ethoxysilane for **16** hours at **125°C** with **0.1** wt % of di-t-butylperoxide.

2. Experimental details

a. Synthesis of bis-(dimethylamino)methylvinylsilane

Methylvinyldichlorosilane, **142.8 g (1.0 mole)**, was dissolved in **1500** ml of benzene in a **3**-liter, round-bottomed, **3**-necked flask fitted with a stirrer, thermometer, reflux condenser, and a gas inlet tube with the outlet about one cm above the surface of the liquid. Dimethylamine was passed in while the benzene solution was being stirred, and the temperature was kept below **30°C**. After ten hours, absorption of dimethylamine had evidently ceased. The mixture was refluxed for three hours, and the benzene was removed by distillation. The product was distilled through a **1.1 x 30**-cm packed fractionating column; the main portion, **72.7 g**, was obtained at **147°C**. It was a clear colorless liquid. The yield of the main portion, b. p. **147°C**, was **46%** of the theoretical; and the total yield of distilled product, assuming the formula of the main fraction, was **65%**. The neutral equivalent of the middle fraction of three that boiled at **147°C**, was **82** (theoretical, **79.2**). The molecular weight, as determined cryoscopically in cyclohexane, was **140**. Hence, the product was bis-(dimethylamino)methylvinylsilane. The analysis is given in Table IV. In view of the correct molecular weight, the correct neutral equivalent, and the inherent difficulty of the silicon determinations, the analysis is considered compatible with the identification.

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4. C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, 1960, p. 401.

5. M. Kanazashi, Bull. Chem. Soc. Japan **28**, 44 (1955); Chem. Abs. **52**, 4556 h (1958).

6. D. G. White and E. G. Rochow, J. Am. Chem. Soc. **76**, 3897 (1954).

7. R. Y. Mixer and D. L. Bailey, J. Polymer Sci. **18**, 573-582 (1955).

Table IV. Analytical Data on Bis-(dimethylamino)methylvinylsilane
and a Polymer Made from It

	Bis-(dimethylamino)-methylvinylsilane		Polymerized with Varox
	Found	Theoretical	Found
Element			
Carbon, %	53.41	53.10	51.56
Hydrogen, %	12.38	11.46	10.70
Nitrogen, %	15.38	17.70	16.38
Silicon, %	14.85	17.74	17.48
Total, %	96.02	100.00	96.12
Neutral equivalent	82	79.2	
Molecular weight	140	158.3	570

b. Polymerization of the vinyl group with peroxides and
sodium and properties of the polymers

When bis-(dimethylamino)methylvinylsilane was stirred with 3%
by weight of benzoyl peroxide or dispersed sodium at 80°C, no visible
change occurred in 15 minutes. However, when the reaction mixtures
were distilled later to recover the vinylsilylamine, a viscous non-
distillable liquid was obtained in each case. The sodium at 80°C
polymerized 38% of the total and the benzoyl peroxide at 80°C
polymerized 25% of the total. In view of the partial success of these
preliminary experiments, a longer polymerization was conducted with
2,5-dimethyl-2,5, di-t-butylperoxyhexane (Varox, R. T. Vanderbilt
Company). Varox is a peroxide that is well known for thermal stability,

and thus is a successful cross-linking catalyst for polyethylene. The monomer, 10 ml (8 g), was refluxed with 0.3 g of Varox. Considerable frothing occurred at first, but it subsided gradually over a period of seven hours. On cooling, the product was a viscous liquid that formed a transparent scum on exposure to air. It was centrifuged to remove the solid, and then it was analyzed to determine whether an appreciable amount of nitrogen had been replaced. The composition is given in Table IV. According to the analysis, refluxing with Varox raised the nitrogen and silicon contents, and so this result is regarded as a case of the inadequacy of the analytical methods. Evidently polymerization occurred largely through the vinyl groups as desired.

The viscous liquid polymer was clear and reddish-orange. Its molecular weight was estimated cryoscopically in cyclohexane to be 570. When spread in a thin film on stainless steel in air, it hardened from the surface inward and within two hours it resembled a varnished surface, except that bubbles were present wherever the film was more than approximately 0.5 mm thick. Subsequently the film became hard and brittle, and it could be peeled away from the stainless steel surface easily. This peeling is in marked contrast to the cured ethylenediamine silazanes, which adhered firmly. After three hours, the film was partially soluble in benzene, but after several days it was no longer soluble in organic solvents. Its thermal stability was fair. Pieces of the transparent straw-colored film exposed to 300°C for 30 minutes became red-brown, hard, and stronger. It approached the strength of glass. We assumed that the film lost most of its nitrogen as it hardened, although this point was not checked.

c. Polymerization of the vinyl group with an azonitrile

Bis-(dimethylamino)methylvinylsilane, 10.0 g (0.063 mole), was placed in a 50-ml, 3-necked flask fitted with a thermometer, stirrer, and reflux condenser, and 0.3 g (0.0018 mole) of 2,2'-azobis(2-methylpropio-nitrile) was added. The mixture was stirred at 90-100°C for 3.5 hours. A second 0.3-g quantity of catalyst was added, and stirring was continued for 1.5 hours at 90-100°C. The temperature was raised to 150-155°C, and stirring was continued for 13 hours. The low-molecular-weight material was then distilled, the final still-pot conditions being 150°C at 10 mm pressure. The residue amounted to 5.3 g. It was a red-brown viscous oil with a molecular weight that was estimated cryoscopically to be 570.

This vinylsilane polymer and the polymer made with Varox were exposed to air in thin films on aluminum and glass at room temperature and at 100°C. All of the films hardened to pale-yellow, brittle solids. They did not adhere well to either glass or aluminum. The odor of dimethylamine was strong while the films were being cured, so it is evident that hydrolysis was taking place. Although the thermal stability of the brittle films was good, their physical character was poor. We concluded that further work was not warranted because of the physical properties of the polymers and the difficulty of obtaining high molecular weights.

d. Polymerization of bis-(dimethylamino)methylvinylsilane with air and ultraviolet light

Three methods in air produced polymers of bis-(dimethylamino)-methylvinylsilane, and all were accompanied by almost complete loss of nitrogen. One clear, colorless, resilient polymer was formed when the vinylsilylamine trickled through a leaky stopcock and was exposed to air. The second polymer, which was also colorless, transparent, and resilient, was formed in air by exposure to ultraviolet light (253.7 mμ) for 24 hours. The third polymer was formed by bubbling air through the monomer for 24 hours. All three polymers were slightly tacky until they were heated at 100°C for an hour. The first two were found to contain 0.2% and 0.4% nitrogen, respectively. The third was not analyzed, but was assumed to be similar to the others.

These polymers did not dissolve in the common organic solvents, acetone, ether, alcohol, and benzene; and they were not visibly affected by water. They did not melt but began to darken and become brittle when heated to 250-350°C. They could be torn easily but had somewhat more strength than the elastomers made from ethylenediamine silazane. They retained their resilience at -78°C in dry ice but not at -195°C in liquid nitrogen.

The ultraviolet source was three General Electric G30T8 sterilizing tubes, which produce a narrow spectrum of light with the peak intensity at 253.7 mμ. Bis-(dimethylamino)methylvinylsilane was exposed to the light in a quartz tube in a nitrogen atmosphere with and without mercury in the liquid. No apparent change in viscosity or color occurred in 65 hours. Evidently ultraviolet light alone will not initiate the polymerization.

D. Reactions of Dimethylsilicondiisocyanate

1. Discussion

Silicon diisocyanates present possibilities for making polymers containing silicon-nitrogen bonds.

$$\equiv SiNCO + H_2N\text{-}R \longrightarrow \equiv Si\overset{H}{N}\text{-}\overset{O}{C}\text{-}\overset{H}{N}\text{-}R, \quad ureas$$

$$\equiv SiNCO + HO\text{-}R \longrightarrow \equiv Si\overset{H}{N}\text{-}\overset{O}{C}\text{-}O\text{-}R, \quad urethanes$$

$$\equiv SiNCO + HN\overset{\diagup Si\equiv}{\diagdown Si\equiv} \longrightarrow -Si\overset{H}{N}\text{-}\overset{O}{C}N\overset{\diagup Si\equiv}{\diagdown Si\equiv}, \quad ureas$$
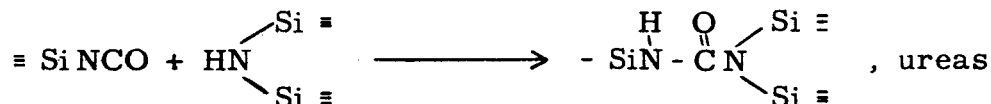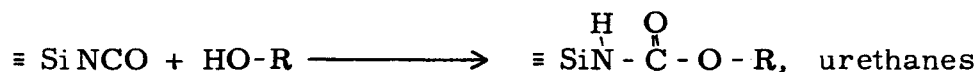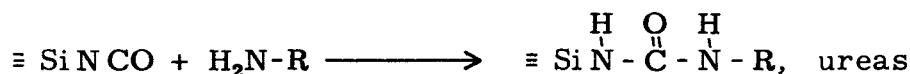
Derivatives of silazanes were previously made with organic isocyanates[1], but they were not stable above 200°C. We hoped the silicon isocyanates would lead to polymers with better thermal stabilities.

In the past program, dimethylsilicondiisocyanate was found to react rapidly with alcohols and amines as expected. When the reactants were mixed, heat was evolved, and white insoluble polymers were formed. A polymer made with ethylenediamine darkened slowly at 210°C, but one made with ethylene glycol darkened only slightly in 30 minutes at 300°C. Because of low solubility in organic solvents, the polymeric derivatives have not been satisfactorily purified and characterized. Unsuccessful attempts were made to induce reactions of the silicon diisocyanate with hexamethylcyclotrisilazane and the silocine made from ammonia and 1,3-dichlorotetramethyldisiloxane (Section II. H. , below). Higher temperatures might force reactions to occur, but these experiments have not yet been made.

Dimethylsilicondiisocyanate evidently formed a polymer when it was treated with methylamine. The product was colorless and transparent, and it became semi-liquid when it was exposed to air for 30 minutes. A similar reaction with ammonia produced a crystalline friable mass. The following reaction may explain the polymer formation with methylamine:

$$
\begin{array}{c}
\quad\quad \text{Me} \\
\text{OCN} - \overset{|}{\underset{|}{\text{Si}}} - \text{NCO} \;+\; \text{MeNH}_2 \;\longrightarrow\; \\
\quad\quad \text{Me}
\end{array}
\left[
\begin{array}{c}
\text{Me} \;\; \text{O} \;\; \text{H} \;\; \text{Me} \;\; \text{H} \;\; \text{O} \\
\; \overset{|}{-\,\text{N}} - \overset{\|}{\text{C}} - \overset{|}{\text{N}} - \overset{|}{\underset{|}{\text{Si}}} - \overset{|}{\text{N}} - \overset{\|}{\text{C}} - \\
\quad\quad\quad\quad\quad \text{Me}
\end{array}
\right]_x
$$
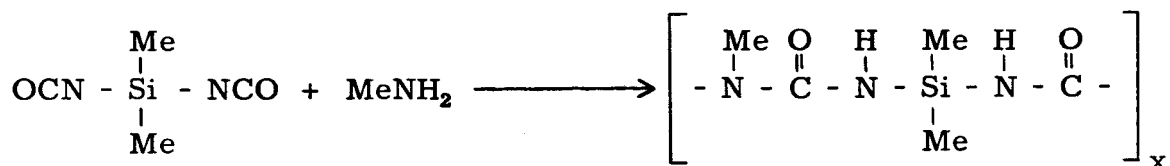
This is a substituted biuret polymer, similar to 1,5-diphenylbiuret, which is known to be formed when ammonia reacts with an excess of phenyl-isocyanate:

$$
2\text{PhNCO} + \text{NH}_3 \;\longrightarrow\; \text{Ph} - \overset{\text{H}}{\underset{|}{\text{N}}} - \overset{\text{O}}{\underset{}{\overset{\|}{\text{C}}}} - \overset{\text{H}}{\underset{|}{\text{N}}} - \overset{\text{O}}{\underset{}{\overset{\|}{\text{C}}}} - \overset{\text{H}}{\underset{|}{\text{N}}} - \text{Ph}
$$
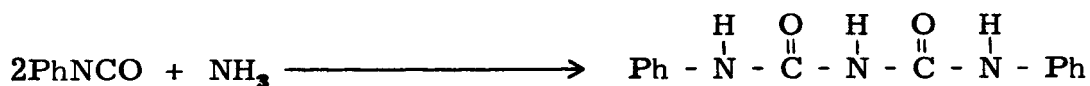
Dimethylsilicondiisocyanate and an excess of methylamine in benzene gave, instead of polymer, N-methylurea, which may have formed as a result of hydrolysis by moisture in the methylamine, or as a result of aminolysis by the excess of methylamine.

$$
\equiv \text{SiNCO} + \text{H}_2\text{NCH}_3 \;\longrightarrow\; \equiv \text{SiNHCONHCH}_3 \xrightarrow{\text{CH}_3\text{NH}_2} \equiv \text{SiNHCH}_3 + \text{H}_2\text{NCONHCH}_3
$$

Dimethylsilicondiisocyanate in benzene treated with the stoichiometric amount of methylamine required to form a polymer gave an insoluble product, melting at 140-160°C, evidently a mixture.

Since isocyanates react with -NH and -OH groups without forming by-products, they might be used for making potting resins. The reactions have not been satisfactorily controlled, however.

2. Experimental details

The method of Forbes and Anderson[8] was used to prepare dimethyl-silicondiisocyanate. Dimethyldichlorosilane, 30 g (0.23 mole), was dissolved in 75 ml of benzene in a 200-ml, 3-necked, round-bottomed flask that was fitted with a magnetic stirrer, thermometer, and reflux condenser. Silver cyanate, 86.9 g (0.53 mole), was added in three portions while stirring. The addition required 25 minutes, and the temperature rose to 79°C. Stirring was continued for ten minutes after the final addition, and the mixture was refluxed on a steam bath for 40 minutes. The silver chloride was removed by filtration and washed with four 35-ml portions of benzene. The filtrate was negative to the Beilstein test. The product was distilled through a 1.2 x 30-cm packed fractionating column. The following three fractions were obtained:

1. B. p. 81-136°C, 6.2 g
2. B. p. 137.5-139°C, 16.0 g
3. Residue, 7.7 g

The molecular weight of Fraction 2 was 150 (theoretical, 146.5), as determined cryoscopically in cyclohexane. Therefore, it was dimethyl-silicondiisocyanate, which was obtained in 49% yield.

Equimolar quantities of the diisocyanate (0.5 g, 0.035 mole) and ethylene glycol (0.22 g, 0.0035 mole) were stirred together in a small bottle in an atmosphere of nitrogen. For about a minute the liquid was clear; then it began to become cloudy, evolve gas, and thicken. In 30 minutes all visible reaction had ceased; the product was a white gummy paste. A second batch was made in the same manner except that the reactants were cooled in ice water before mixing, and immediately after

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8. G S. Forbes and H. H. Anderson, J. Am. Chem. Soc. 70, 1222-1223 (1948).

mixing they were cooled in a dry-ice acetone bath. Apparently little or no reaction occurred until they were warmed to room temperature. Then the mixture became slightly warm and thickened to a paste as before, except that no evolution of gas was seen. When placed in an oven, the second product did not change visibly in an hour at 100°C and 30 minutes at 200°C. In an hour at 250°C the paste became crumbly. In 15 minutes at 300°C the hardened paste began to turn yellow.

A similar but faster reaction occurred with ethylenediamine, and the product was evidently less stable to heat. When equimolar quantities of dimethylsilicondiisocyanate and ethylenediamine were mixed, they reacted so fast that the mass solidified in a few seconds. The diisocyanate (0.5 g, 0.0035 mole) was dissolved in 5 ml of benzene and 0.21 g (0.0035 mole) of dry ethylenediamine was added and stirred. In about two minutes cloudiness appeared, the mixture became warmer, and it solidified in three minutes. The product was rolled into a waxy ball. Evidently some of the benzene was trapped in the polymer, but the appearance of the product did not change appreciably when it was left exposed in air for four hours. The melting point was 197°C. Heating for an hour at 100°C caused no change. A sample was kept molten at 220°C for an hour, and on cooling no change was detected. It bubbled slightly without other evidence of decomposition at about 210°C.

Dimethylsilicondiisocyanate appeared to react partially with hexamethylcyclotrisilazane. On mixing a cloudy liquid was formed. Solid formed progressively over a period of 15 hours, but the final product was a semi-solid paste. The possibility exists that water entered the reaction, and consequently the experiment is considered inconclusive.

No reaction was observed when dimethylsilicondiisocyanate was mixed with 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclo-octasilane (Section II.H., Figure 1, Compound A). Forcing conditions were not used.

When methylamine was passed through dimethylsilicondiisocyanate the liquid gradually thickened and within a minute was too viscous to be stirred. Fibers could be drawn from the colorless, transparent, hygroscopic product.

In a second experiment, 4. 0 g (0. 028 mole) of dimethylsilicon-diisocyanate was dissolved in 15 ml of benzene in a 50-ml, 3-necked round-bottomed flask fitted with a stirrer, reflux condenser, thermometer and gas inlet tube below the surface of the liquid. The solution was cooled to 8°C in an ice-water bath, and methylamine was passed in slowly with stirring. In 9 minutes there was no evidence of reaction, and then the temperature rose rapidly to 33°C and a few small crystals appeared. The temperature continued to rise to 46°C, and then there were no crystals visible. Introduction of methylamine was continued; and when the temperature dropped to 30°C, the mixture became thick with crystals. The addition of 5 ml of benzene failed to make stirring possible; consequently the ice bath was replaced by a heating mantle, and the mixture was refluxed for 25 minutes while methylamine was passed in. After standing overnight, the crystals were removed by centrifugation and recrystallized four times from purified dioxan. The crystals melted at 103. 5-104. 5°C. On standing in air there was no evidence of decomposition. The crystals were shown to be N-methylurea (reported m. p. 101-102°C)[9] by elemental analysis (Table V). N, N'-dimethylurea, m. p. 102°C[10] was also a possibility disproved by the analysis.

It is difficult to overlook the possibility that moisture in the methylamine caused rupture of the Si-N bond. However, the care used in the experiment seems to preclude that possibility and suggests a more subtle mechanism such as aminolysis.

$$\equiv SiNCO + H_2NCH_3 \longrightarrow \ \equiv SiNHCONHCH_3 \xrightarrow{CH_3NH_2} \equiv SiNHCH_3 + H_2NCONHCH_3$$

9. C. E. Fawsitt, J. Chem. Soc. 85, 1583 (1904.

10. O. Degner and H. v. Pechman, Ber. 30, 651 (1897).

Table V.   Compound Made from Methylamine and Dimethylsilicondiisocyanate

	Found	Theoretical		
		$C_3H_8N_2O$ [a]	$C_6H_{16}N_4O_2Si$ [b]	$C_2H_6N_2O$ [c]
Carbon, %	32.68	40.89	35.27	32.42
Hydrogen, %	8.34	9.15	7.89	8.16
Nitrogen, %	37.91	31.80	27.43	37.82
Silicon, %	2 ±1	-	13.75	-
Oxygen, % (by difference)	19 ±1	18.16	15.66	21.60
Melting point, °C	103.5-104.5			

[a] N,N'-dimethylurea, $CH_3NHCONHCH_3$

[b]

$$CH_3\overset{H}{N}-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-\overset{\overset{CH_3}{|}}{\underset{CH_3}{Si}}-\overset{H}{N}-\overset{\overset{O}{\|}}{C}-\overset{H}{N}CH_3$$
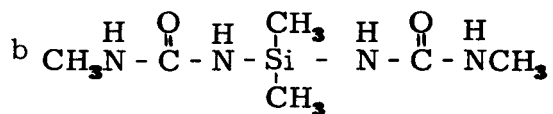
[c] N-methylurea, $C_2H_6N_2O$

E. Silazane Polymer from a Trifunctional Silane

1. Discussion

Trifunctional chlorosilanes offer a means of introducing branching into silazane polymers that have usually been made by the reaction of a difunctional chlorosilane with a difunctional amine. A trifunctional silane might also interfere with cyclization, which has been the main obstacle in the past to the formation of linear silazane polymers of high molecular weight. The trifunctional silane that was used evidently had the desired effect, and the polymeric product had the degree of thermal stability that is typical of the silazanes.

Comparative experiments were made to determine the effect of a trifunctional silane when added to a reaction mixture containing difunctional silanes. The common procedure for the synthesis of hexamethylcyclotrisilazane was used. In that procedure, ammonia is added to a stirred solution of dimethyldichlorosilane in benzene. In the two experiments to be described, methyltrichlorosilane was substituted for 10% and 50% of the dichlorosilane. There was some increase in the amount of polymer when 10% of the trifunctional silane was used and more when 50% was used. The polymeric product was hard and thermoplastic. When heated, it apparently polymerized to a brittle solid with exceptional thermal stability. The data on yields of polymer in the three reactions are in Table VI and the elemental composition of the polymer made from the 1:1 mixture of di- and tri-functional silanes is given in Table VII.

The elemental analysis suggested that the formula shown in footnote a, Table VII, was reasonable except that approximately one of every four nitrogen atoms had been replaced by oxygen.

A blend of the "di-tri" silazane with the ethylenediamine silazane had no outstanding properties, but the possibilities were not investigated in detail. A blend of the "di-tri" silazane with nonamethylcyclotrisilazane was examined for lubricity, but the results were not encouraging, as reported below in Section VII.

Table VI. Polymerization by Use of Methyltrichlorosilane in a
Silazane Synthesis

	Amount distillable, % of product	Amount not distillable, % of product
A standard synthesis of hexamethylcyclotrisilazane (Dimethyldichlorosilane plus ammonia)	99	1
Methyltrichlorosilane and dimethyldichlorosilane (1:9)	73	27
Methyltrichlorosilane and dimethyldichlorosilane (1:1)	10	90

Table VII. Elemental Composition of Silazane Made with an Equimolar
Mixture of Di- and Trifunctional Silicon Halides

Element	Found, %	Theoretical, %[a]
Carbon	25.59	24.62
Hydrogen	7.48	8.26
Nitrogen	20.19	28.73
Silicon	38.35	38.39
Remainder (presumably oxygen)	8.39	

Formula for calculations of theoretical composition: $C_3H_{12}Si_2N_3$

$$\left[\begin{array}{cccc} \quad CH_3 & H & CH_3 & \\ - \; Si & - \; N & - \; Si & - \; NH \; - \\ \quad CH_3 & & NH & \end{array} \right]_x$$
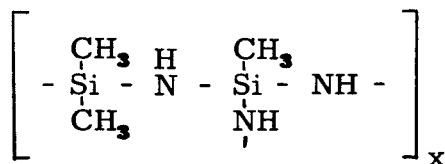
2. Experimental Details

a. With 10% trifunctional silicon halide

In a 5-liter, 3-necked flask fitted with a stirrer, reflux condenser, thermometer, and gas inlet tube (exit maintained just above the surface of the liquid) were placed 2800 ml of benzene, 116.1 g (0.9 mole) of dimethyl-dichlorosilane, and 14.9 g (0.1 mole) of methyltrichlorosilane. The solution was stirred and ammonia was passed over the surface for 45 minutes with the temperature kept below 50°C. When the heat of reaction became undetectable, a balloon was placed on the condenser outlet, and the ammonia flow was adjusted to keep it inflated. Stirring was continued under these conditions for an hour. After standing overnight, the mixture was refluxed for three hours, cooled, and filtered. The clear liquid was negative to the Beilstein test. The product was placed in a fractionating column, and 35.2 g, mostly hexamethylcyclotrisilazane, was distilled below 53°C at 0.6 mm. At this point the pot temperature was 140°C. The undistillable residue was 16.8 g of a viscous brown oil. Thus the total yield was 71% of theoretical if $-(CH_3)_2SiNH-$ is considered to be the repeating unit. Octamethylcyclotetrasilazane was detected in the distillable portion, but it was not isolated. The data are summarized in Table VI. The neutral equivalent of the residue was 87. This figure may be compared with the theoretical neutral equivalents of these two possible species:

$-Si(CH_3)_2-NH-$; neutral equivalent, 73.2

$-Si(CH_3)_2-NH-SiCH_3(NH)_2<$; neutral equivalent, 48.8

Evidently hydrolysis was incomplete or there was oxygen in the product.

b. With 50% trifunctional silicon halide

The synthesis using 50% methyltrichlorosilane was conducted in the same manner as the reaction just described. Dimethyldichlorosilane, 64.5 g (0.5 mole), and methyltrichlorosilane, 74.7 g (0.5 mole), were dissolved in 2800 ml of benzene. Only 5.1 g of the product was distillable. The residue, 47.7 g, did not distill at a pot temperature of 190°C and a pressure of 0.6 mm. The neutral equivalent of the residue was 79. The data, including elemental composition, are summarized in Tables VI and VII.

The "di-tri" silazane was blended with ethylenediamine silazane in a 1:5 mixture. The two, in a test tube, were mixed by gentle heating and stirring. After standing overnight, the mixture was heated in an oven at 400°C for two hours. The mixture remained liquid at 400°C but became resilient on cooling to room temperature. The mixture was then exposed to 14.2 megaroentgens of gamma radiation over a 66-hour period, whereupon it became tacky again. Heating in an oven at 100°C for an hour produced a non-tacky resilient solid. After being heated at 400°C for 30 minutes, the product closely resembled the cured ethylenediamine silazanes except that it was slightly less foamed and more easily crushed.

F. Attempts to Synthesize a Silylfluoroamine

1. Discussion

The object of synthesizing a fluorinated aminosilane was to determine the effect of fluorine substitution on hydrolytic and thermal stabilities. The fluorine atoms, being strongly electronegative, were expected to reduce the electron density around the nitrogen atom, thereby reducing the susceptibility of the silicon-nitrogen bond to attack by acids and water. The fluoroamine chosen for synthesis was 2,2,3,3,3-pentafluoropropylamine, because it appeared to be the one obtainable with the least effort. Two unsuccessful attempts were made to convert it to a silyl derivative. Apparently some type of reaction occurred between the amine and trimethylchlorosilane, but none of the desired product was isolated.

According to the literature usually only one trimethylchlorosilane molecule reacts with an amine. The reason is presumably steric hindrance. Sauer and Hasek[11] obtained only N-(trimethylsilyl)methylamine and not the disilyl derivative when they treated trimethylchlorosilane with methylamine. Apparently they made no specific attempt to force the reaction of another silicon halide molecule. Speier, Zimmerman, and Webster[12] refluxed

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11. R. O. Sauer and R. H. Hasek, J. Am. Chem. Soc. 68, 241-244 (1946).

12. J. L. Speier, R. Zimmerman, and J. Webster, J. Am. Chem. Soc. 78, 2278-2281 (1956).

N-(trimethylsilyl)allylamine (b. p. **109. 5°**C at **731** mm) overnight with ammonium sulfate and produced N, N'-bis(trimethylsilyl)allylamine (b. p. **179°**C at **741** mm). Accordingly we expected either or both the monosilylamine or the disilylamine to be produced, but we saw no evidence of either in careful fractional distillation.

2. Experimental details

a. Preparation of 2, 2, 3, 3, 3-pentafluoropropylamine

2, 2, 3, 3, 3-Pentafluoropropylamine was prepared by the method of Husted and Ahlbrecht.[13] Lithium aluminum hydride, **28. 5** g, was stirred with **445** ml of absolute ether in a **500**-ml flask, refluxed for an hour, and then cooled and filtered through a sintered glass filter under nitrogen pressure. An aliquot of the filtered solution, **5. 0** ml, was pipetted into a beaker, and the ether was allowed to evaporate. Dry ethanol was added dropwise to decompose the hydride, water was added, and the resulting mixture was titrated electrometrically with standard hydrochloric acid. On the assumption that all of the titratable base was derived from the lithium in lithium aluminum hydride, the ether solution was found to contain **0. 057** g of $LiAlH_4$/ml.

The ether solution (**203** ml, containing **11. 6** g, **0. 306** mole , of $LiAlH_4$) was placed in a **1**-liter, **3**-necked flask fitted with a magnetic stirrer, dropping funnel, and a condenser cooled by dry ice-acetone. Pentafluoropropionamide, **25** g (**0. 153** mole), in **114** ml of ether was added dropwise with stirring at a rate that maintained gentle reflux. After addition was complete, the solution was stirred for three hours. Then it was cooled in a dry ice-acetone bath, and **17** ml (**0. 95** mole) of water was added with stirring. With continued cooling and stirring, **45. 5** ml (**0. 82** mole) of concentrated sulfuric acid was added. At this point **200** ml of ether was added to facilitate stirring. The cooling bath was removed, and the solution was stirred for **30** minutes. The solution was filtered, and the white crystalline mixture of amine sulfates was dried in air overnight and then in an oven at **65°**C for **30** minutes.

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13. D. R. Husted and A. H. Ahlbrecht, <u>J. Am. Chem. Soc.</u> **75,** **1605-1608** (1953).

The dried product was placed in a 500-ml, 3-necked flask fitted with a stirrer, distillation condenser, and dropping funnel. The receiver was immersed in ice, and a dry-ice trap was placed downstream from it. A solution of 73.5 g (1.83 moles), of sodium hydroxide in 79 ml of water was added dropwise with stirring. The flask was heated, and 20.4 g of liquid was distilled over a range of 35-80°C. The distillate was then fractionated in a straight glass column measuring 36 x 0.25 cm (I.D.). The portion boiling from 47-49°C was 12.2 g (0.082 mole), 53% of the theoretical yield.

To dry the pentafluoropropylamine, about 0.7 g of solid potassium hydroxide was added. Unexpectedly, after standing for several days in a refrigerator, a voluminous white precipitate formed. Evidently the alkali had reacted with the amine. To recover the amine, the mixture was poured into cold water, neutralized with hydrochloric acid while cooling in ice, and evaporated to recover the hydrochloride. At this point several grams of amine hydrochloride obtained from previous syntheses was added, and the amine was regenerated by addition of alkali and distillation. The total amount of amine, b.p. 44-49°C, was 15.3 g. In subsequent preparations drying was not attempted except by distillation.

b. Reaction of the fluoroamine with trimethylchlorosilane—first method

2,2,3,3,3-Pentafluoropropylamine was treated with trimethylchlorosilane by the method described below. Triethylamine was used in the procedure in an effort to conserve the fluoroamine and increase the yield of fluoroaminosilane. The initial step of the reaction was expected to follow this equation:

$$3\ RNH_2 + 2\ Me_3SiCl \longrightarrow RN(SiMe_3)_2 + 2\ RNH_2 \cdot HCl$$
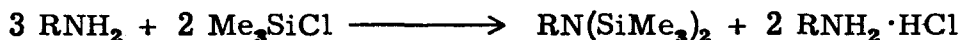
Only $\frac{1}{3}$ of the amine would be converted to fluoroaminosilane. Triethylamine, being a stronger base than the fluoroamine, was expected to liberate the amine in the second step of the reaction in this manner:

$$2\ RNH_2 \cdot HCl + 2\ Et_3N \longrightarrow 2\ Et_3N \cdot HCl + 2\ RNH_2$$
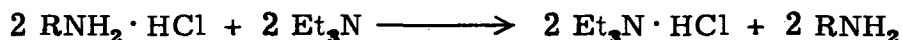
In the third step, which was a repetition of the first but in smaller amounts, $1\frac{1}{3}$ mole of silicon halide was expected to produce $\frac{2}{3}$ mole of fluoroaminosilane. Even if the triethylamine failed to function as expected, there was thought to be little likelihood of losing the fluoroaminosilane formed in the first step. Accordingly, the reaction was run in five steps followed by adding a small amount of triethylamine to reduce the excess of silicon halide.

The procedure was carried out as follows in a 500-ml, 3-necked flask fitted with a reflux condenser, magnetic stirrer and dropping funnel.

First step:

2,2,3,3,3-Pentafluoropropylamine, 15.3 g (0.102 mole), in 50 ml of benzene was added dropwise with stirring to 7.4 g (0.069 mole) of trimethylchlorosilane in 200 ml of benzene while the temperature was kept below 30°C. The mixture was stirred for two hours and then allowed to stand overnight. The white insoluble matter appeared gelatinous, and it settled only partially.

Second step:

Triethylamine, 7.0 g (0.069 mole), was added with stirring while the temperature was kept below 30°C. The mixture was then stirred at room temperature for two hours and allowed to stand three hours.

Third step:

Trimethylchlorosilane, 4.95 g (0.046 mole), in 50 ml of benzene was added as in Step 1.

Fourth step:

Triethylamine, 4.65 g (0.046 mole), was added as in Step 3.

Fifth step:

Trimethylchlorosilane, 3.3 g (0.031 mole), in 50 ml of benzene was added as in Step 1.

Sixth step:

Triethylamine, 0.5 g (0.005 mole), was added, and the mixture was refluxed for 30 minutes. There was evidently an excess of halide present. Accordingly, 1.0 g (0.01 mole) of trimethylamine was added, and the mixture was again refluxed for 30 minutes. At this point the total of reactants was as follows:

> 2,2,3,3,3-pentafluoropropylamine, 15.3 g
> (0.102 mole)
> trimethylchlorosilane, 15.65 g (0.146 mole)
> triethylamine, 13.15 g (0.130 mole)

The insoluble material was removed by centrifugation, and the solid was washed with 100 ml of benzene. Evaporation of a small sample of the clear liquid produced a large amount of needle-like crystals that were believed to be mainly a compound of triethylamine and the silicon halide.

The benzene was removed by distillation, and the vapor temperature rose above 80°C when approximately 5 g remained in the still pot. However, no satisfactory fractions were obtained, and the residue was a dark brown oil that would not distill at 200°C.

Evidently there was no merit in the complicated reaction scheme that was used. In the next attempt, the triethylamine was not used.

c. Reaction of the fluoroamine with trimethylchlorosilane— second method

Trimethylchlorosilane, 89.9 g (0.83 mole), was dissolved in 250 ml of benzene in a 500-ml, 3-necked flask fitted with a dropping funnel, stirrer, thermometer, and reflux condenser. 2,2,3,3,3-Pentafluoropropylamine, 20.4 g (0.138 mole), was mixed with 70 ml of benzene and added slowly through the dropping funnel. The temperature rose from 25°C to 27.5°C and the solution became cloudy. Stirring was continued for 6.5 hours while the temperature remained at 27.5°C. The mixture stood overnight. On the next day the temperature of the mixture was raised to 40°C and held there while stirring for two hours. The mixture was then refluxed for four hours while the vapor temperature was 58°C, the boiling point of trimethylchlorosilane. In spite of care to exclude moisture, a gel collected in the condenser. Distillation was started in a clean condenser, and a foamed gel appeared again. Accurate observation of the distillation temperature was difficult because of the gel, but apparently it remained in the range of 75-80°C. After about half of the benzene had been distilled, the undistilled portion was cooled, freed of a white solid by filtration, and distilled in a 1.2 x 30-cm fractionating column. The temperature remained at 80°C until the pot was almost completely dry. About 5 ml of a black liquid drained out of the column. The previously distilled fractions were filtered and redistilled in the fractionating column. Additional quantities of solid formed in the still head. The vapor temperature ranged from 67-80°C, and no fractions that appeared to be the fluoroaminosilane were obtained. However, any desired product that boiled in the range of 58-80°C would probably have been overlooked. We have no simple satisfactory explanation of the formation of the solid in the still head, but we have observed a solid often when unreacted silicon halide was present. In this case it may have been complicated by the presence in the reaction mixture of unstable reaction products.

G. Addition Compounds Made from Hexamethylcyclotrisilazane and Silicon Tetrafluoride

1. Discussion

Hexamethylcyclotrisilazane was treated with silicon tetrafluoride in an attempt to reduce the instability of the silazane by formation of an addition compound. Steric and electronic factors are both involved. Although Pfleger[14] and Weiss[15] in collaboration with Rochow observed that coordination of silazanes with metals did not improve stability, we wished to determine whether silicon tetrafluoride would add to the silazane and what the thermal behavior of the product would be.

Silicon tetrafluoride is known to combine with ethylenediamine[16] in a 1:1 ratio and with trimethylamine[17] in either a 1:1 or a 1:2 ratio to form relatively stable compounds. The mechanism is thought to be addition of the lone pair of electrons on the nitrogen atom to the d-orbitals of the silicon atom. There is evidently no tendency toward dehydrohalogenation to produce hydrogen fluoride from the complex with ethylenediamine.

Silicon tetrafluoride did form an addition compound with hexamethylcyclotrisilazane. The product was a viscous liquid that was quite sensitive to the moisture in air. Analysis showed that approximately one SiF_4 molecule was attached to each hexamethylcyclotrisilazane molecule (Table VIII). When the liquid was heated

14. H. Pfleger, "A Contribution to the Chemistry of Silylamines and Silazanes," Technical Report on Contract Nonr-1866 (13), Chemistry Branch, Office of Naval Research, E. G. Rochow, Project Director.

15. R. Weiss, "Coordination of Silicon-Nitrogen Compounds," Technical Report on Contract Nonr-1866 (13), Chemistry Branch, Office of Naval Research, E. G. Rochow, Project Director.

16. W. C. Schumb and P. S. Cook, J. Am. Chem. Soc. 75, 5133 (1953).

17. C J. Wilkins and D. K. Grant, J. Chem. Soc., 927 (1953).

Table VIII. Addition Compounds Made from Hexamethylcyclotrisilazane
and Silicon Tetrafluoride

	Found		Theoretical		
	Unheated sample, A	Heated sample, B	C $C_2H_7F_4NSi_2$	D $C_4H_{14}F_4N_2Si_3$	E $C_6H_{21}F_4N_3Si_4$
Carbon, %	16.59	9.76	13.55	19.18	22.27
Hydrogen, %	4.86	3.25	3.98	5.63	6.54
Fluorine, %	25.10	20.25	42.88	30.35	23.48
Nitrogen, %	14.82	14.38	7.90	11.19	12.99
Silicon, %	37.15	40.40	31.69	33.65	34.72
Total, %	98.52	88.04	100.00	100.00	100.00

A. Viscous liquid product as obtained.

B. Foamed solid obtained by heating Sample A.

C. One SiF_4 unit for each $-SiMe_2NH-$ unit.

D. One SiF_4 unit for each pair of $-SiMe_2NH-$ units.

E. One SiF_4 unit for each hexamethylcyclotrisilazane molecule.

strongly in a nitrogen atomsphere, it solidified while boiling to a brown brittle transparent solid that appeared to be extremely stable to heat, because it could not be changed appreciably by heating. However, the sample emitted enough gas when heated for 1.5 hours at 450°C in a sealed tube for it to be classed as low in thermal stability. This method of estimating thermal stability was described previously.[1]

2. Experimental details

The addition compound of hexamethylcyclotrisilazane and silicon tetrafluoride was made as follows. In a 300-ml, 3-necked flask fitted with a reflux condenser, thermometer, magnetic stirrer, and gas-inlet tube were placed 100 ml of benzene and 10 g (0.046 mole) of hexamethylcyclotrisilazane. Silicon tetrafluoride was passed in slowly for one hour through the gas-inlet tube, which was approximately three cm above the surface of the stirred liquid. A positive pressure of silicon tetrafluoride was kept on the stirred solution by means of a balloon for an additional hour. The weight increase of the reaction vessel was 6.2 g or 0.059 moles of silicon tetrafluoride. The solution was refluxed for three hours. At this point the solution was dirty yellow in color with a small amount of brown flocculated material in suspension.

The liquid product was centrifuged to clarify it. Thereafter, samples of the liquid were evaporated at reduced pressures to obtain the product without exposure to air. The product was a viscous yellow-brown liquid. It formed a brittle scum immediately on exposure to air and smelled strongly of ammonia. When it was heated in a nitrogen atmosphere in a Pyrex flask, it boiled and then solidified while boiling to a hard brittle transparent solid that did not adhere to the glass. This lack of adhesion is in marked contrast to the performance of the other silazanes. This solid did not visibly decompose when heated on a spatula held in the hottest flame of a Meker burner. The product was suspected of being inorganic until the analytical results were obtained.

The analytical results were used to calculate probable formulas, but it was evident that the data did not fit any obvious formulas exactly. The elemental ratios in the liquid product, assuming silicon to be 1.0, were the following:

C	:	H	:	F	:	N	:	Si
1.05		3.66		1.0		0.8		1.0

If one silicon tetrafluoride molecule were attached to each hexamethyl-cyclotrisilazane molecule, the elemental ratios would be:

C	:	H	:	F	:	N	:	Si
1.5		5.25		1.0		0.75		1.0

Thus the F:N:Si ratios agree well with the hypothesis that one silicon tetrafluoride molecule is attached to one hexamethylcyclotrisilazane molecule. However, the carbon-hydrogen values do not agree. The elemental ratios found in the pyrolyzed product were:

C	:	H	:	F	:	N	:	Si
0.56		2.26		0.74		0.71		1.0

In view of the refractory character of the pyrolyzed polymer, it is not surprising that the total of the elemental compositions does not equal 100%. It is unlikely that oxygen or moisture was introduced inadvertently.

A sample of the polymer produced by pyrolysis was heated in a sealed evacuated Pyrex tube for 1.5 hour at 450°C. After cooling, the tube was opened under water and the gas produced was found to be 2.2 ml/g of solid. This large amount of gas implies less thermal stability than most of the other silazanes and siloxanes. The results of this experiment should be confirmed.

H. Silicon-Nitrogen Compounds Derived from Silicon Oxychlorides

1. Discussion

There are several possible advantages in using silicon oxychlorides as starting materials for compounds containing silicon-nitrogen bonds. One is that the tendency to form ring compounds instead of polymers may be reduced. Another is that the chain, $- N - Si - O - Si_{7}$ may have inherently good properties in terms of stability, adhesion, and coordination. Another is that an eight-membered ring, if formed, would be a difunctional silicon-nitrogen cyclic compound, thereby affording the opportunity to make linear polymers by connecting the rings.

The silicon oxychlorides, which were made by known methods,[18] had the general formula:

$$Cl - \left[Si(CH_3)_2 - O \right]_n \quad Si(CH_3)_2 Cl$$
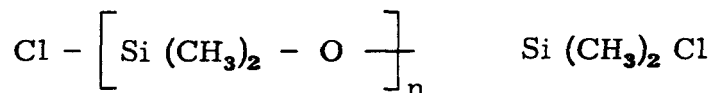
The chlorosiloxanes with n - 1 and n - 2 were treated with ammonia and methylamine. The only identifiable pure product of four reactions was obtained from the reaction of 1, 3-dichlorotetramethyldisiloxane, n - 1, with ammonia. The product was identified as 2, 2, 4, 4, 6, 6, 8, 8-octamethyl-1, 5-dioxa-3, 7-diazacyclooctasilane. The formula is given as "A" in Figure 1. This compound was first reported by Sokolov,[19] who did not mention its thermal stability. We found its stability to be the highest of any compound we have yet prepared, except for the polymer made from silicon tetrachloride and methylamine. Possible formulas of the other compounds made with silicon oxychlorides are shown in Figure 1.

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18. W. Patnode and D. F. Wilcock, J. Am. Chem. Soc. 68, 359 (1946).

19. N. N. Sokolov, Zhur. Obshchei Khim. 29, 258-263 (1959); Chem. Abs. 53, 21622 d (1959).
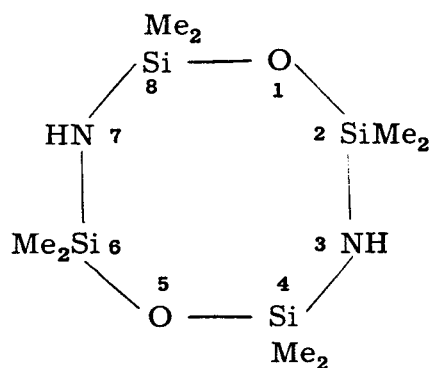
2, 2, 4, 4, 6, 6, 8, 8-Octamethyl-1, 5-
dioxa-3, 7-diazacyclooctasilane

A
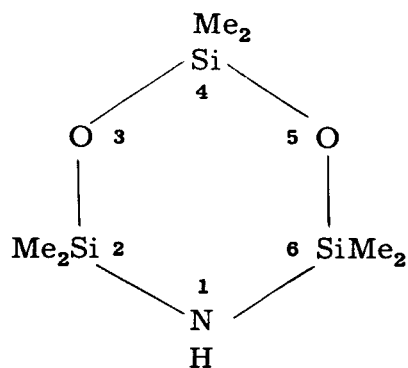
2, 2, 4, 4, 6, 6-Hexamethyl-3, 5-
dioxa-1-azacyclohexasilane

B
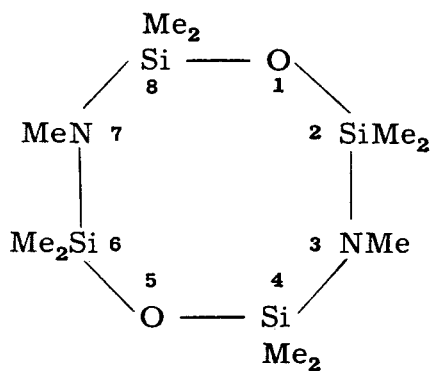
2, 2, 3, 4, 4, 6, 6, 7, 8, 8-Decamethyl-
1, 5-dioxa-3, 7-diazacyclooctasilane

C
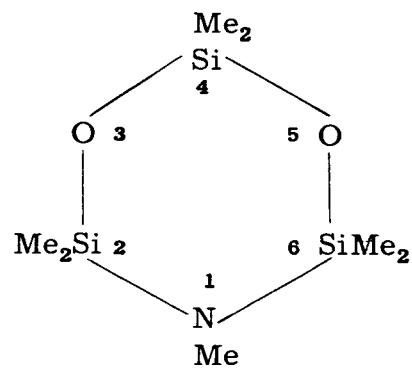
1, 2, 2, 4, 4, 6, 6-Heptamethyl-
3, 5-dioxa-1-azacyclohexasilane

D

Figure 1. Cyclic Silicon-Oxygen-Nitrogen Compounds

The second reaction, 1, 5-dichlorohexamethyltrisiloxane, n = 2, with ammonia, formed some polymer. About one-third of the product distilled readily, but the remainder did not distill at 225°C at 3 mm pressure. If the six-membered ring formed as shown in Figure 1 B, there was not much of it. Later when the product was boiled in an open test tube, some evolution of gas occurred at about 100°C; and as boiling was continued, the temperature of the liquid eventually reached 500°C. When it cooled to room temperature, the liquid had approximately the viscosity of a heavy oil, and it did not crystallize on standing. The initial low boiling point probably resulted from partial hydrolysis or condensation of end-amino groups. A liquid of this type might be useful where fluidity over a wide temperature range is desired.

Both of the chlorosiloxanes just mentioned were treated with methylamine. 1, 3-Dichlorotetramethyldisiloxane yielded a compound that was probably 2, 2, 3, 4, 4, 6, 6, 7, 8, 8-decamethyl-1, 5-dioxa-3, 7-diazacyclooctasilane, Figure 1 C. The purity may have been poor, because the molecular weight and the elemental analysis were not close enough to the theoretical values. The thermal stability at 450°C in a sealed tube was disappointing. It was approximately in the stability range of octamethylcyclotetrasilazane and octamethyl-cyclotetrasiloxane.

The product made from methylamine and 1, 5-dichlorohexa-methyltrisiloxane was a mixture that was not separated into any pure products. On the first attempt at fractional distillation at 30 mm pressure, decomposition occurred at about 60°C, and no fractions boiling over a narrow temperature range were obtained. Heating the undistilled residue in an open tube produced a liquid boiling at 400°C which remained liquid on cooling. Evidently, the initial product contained end-amino groups that condensed on heating to release methylamine.

Interest in the silicon-nitrogen compounds made from chloro-siloxanes centers around three of their characteristics. One is that the eight-membered ring, Figure 1 A, has only two reactive centers, whereas the cyclic silazanes have at least three. The two reactive centers suggest linear polymerization with difunctional reagents. The second point of interest is the high thermal stability of the cyclic silicon-oxygen-nitrogen compounds, although only one of these compounds was purified sufficiently to permit an evaluation of stability. The third is the existence of these compounds in the liquid state over extraordinary temperature ranges.

2. Experimental details

Silicon oxychlorides were made by the method of Patnode and Wilcock.[18] In a 1-liter, 3-necked flask, fitted with a dry ice-acetone reflux condenser, stirrer, and dropping funnel, were placed 260 g (2. 01 moles) of dimethyldichlorosilane and 150 ml of dry ether. In the funnel, which had its outlet below the surface of the liquid, were placed 18 g of water (1. 0 mole) and 18 ml of dioxane. The water-dioxane solution was added slowly with stirring over a period of 45 minutes while the ether refluxed gently. The product was distilled through a packed 1. 2 x 30-cm column. The 1,3-dichlorotetramethyldisiloxane fraction (35. 2 g) distilled at 137-138°C. The 1, 5-dichlorohexamethyltrisiloxane (19. 7 g) distilled at 182-184°C.

1, 3-Dichlorotetramethyldisiloxane was treated with ammonia by a method similar to the one used to prepare silazanes. In a 1-liter, 3-necked flask fitted with a stirrer, reflux condenser, and gas inlet tube were placed 35. 2 g (0. 173 mole) of the disiloxane and 350 ml of benzene. Stirring was started and ammonia was passed in through the inlet tube, which was about 2. 5 cm above the surface of the liquid. A white precipitate formed, and the temperature rose to 48°C in 1. 8 hour and then dropped to 25°C in a total of 3. 5 hours. The solution was refluxed for three hours. After cooling, the Beilstein test of the supernatant liquid was negative. After standing overnight, the solution was filtered, and then distilled in a 1. 2 x 30-cm fractionating column to give a crystalline fraction (9. 3 g) boiling at 106-107°C at 26 mm. The undistilled portion (10. 1 g) may have contained material similar to the distilled portion. The total yield was 19. 4 g, 77% of the theoretical yield, when -NH-SiMe$_2$-O-SiMe$_2$- is taken as the formula.

The distilled product melted at 34-36°C after recrystallization from Skellysolve "B". Other data are listed in Table IX. The properties agree reasonably well with those reported by Sokolov.[19]

Table IX. Characteristics of the Product Obtained from the Reaction of
Ammonia with 1, 3-Dichlorotetramethyldisiloxane

Analysis	Found	Theory[a]
Carbon, %	31.50	32.60
Hydrogen, %	8.47	8.89
Nitrogen, %	8.46	9.50
Silicon, %	33.60	38.14
Remainder, % oxygen	17.97	10.87
Neutral equivalent	167	147.3
Molecular weight (cryoscopic in cyclohexane)	270	294.7

Gas produced at 450°C in 1.5 hr, 0.19 ml per gram.[b]

Boiling point, 106-107°C at 26 mm.

Melting point, 34-36°C.

---

[a] For the formula:

$$\begin{array}{c} \mathrm{Me_2} \\ \nearrow \mathrm{Si} - \mathrm{O} \searrow \\ \mathrm{HN} \qquad\qquad \mathrm{SiMe_2} \\ | \qquad\qquad\qquad | \\ \mathrm{Me_2Si} \qquad\qquad \mathrm{NH} \\ \searrow \mathrm{O} - \mathrm{Si} \nearrow \\ \mathrm{Me_2} \end{array} \qquad C_8H_{26}N_2O_2Si_4$$
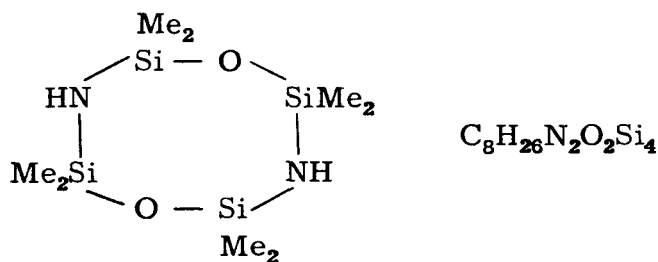
[b] 0.1566 g heated in a 4.5-ml sealed tube at 450°C for 1.5 hr. The gas
produced was measured over water. This is comparable to 0.82 ml
per gram from octamethylcyclotetrasiloxane and 0.24 ml per g from
nonamethylcyclotrisilazane. For additional data see page 11, Report 14
(February 20, 1961), Contract No. DA-01-009-506-ORD-829, ID No.
0602-00-60 to the U. S. Army Ballistic Missile Agency.

1,5-Dichlorohexamethyltrisiloxane was treated with ammonia in the following manner. In a 1-liter, 3-necked flask fitted with a stirrer, thermometer, reflux condenser, and gas inlet tube (about an inch above the surface of the liquid) were placed 250 ml of benzene and 19.7 g (0.071 mole) of the dichlorotrisiloxane. Ammonia was passed in for 15 minutes while the liquid was stirred, and the temperature rose to 48°C. A positive pressure of ammonia was maintained with the aid of a balloon while stirring was continued for two hours. The liquid was then at room temperature. It was refluxed for three hours, and then it stood overnight. The clear supernatant solution was negative to the Beilstein test. The ammonium chloride was filtered off. The amount was 7.1 g, whereas the theoretical value was 7.5 g. The benzene was distilled through a 1 x 30-cm packed column and then three fractions of the product were obtained:

1.	B. p. 62-63°C at 29 mm	1.8 g
2.	B. p. 47°C at 3 mm	1.0 g
3.	Residue, pot at 225°C at 3 mm	6.2 g
		9.0 g

The still residue was boiled in an open test tube, several weeks after the original distillation, to determine the maximum temperature at which it was liquid. It began to evolve some gas at 100°C, probably as a result of hydrolysis; but after heating for a few minutes, the liquid was boiling at 500°C. On cooling to 0°C it remained liquid with the viscosity of a heavy oil.

Methylamine reacted with 1,3-dichlorotetramethyldisiloxane in the following manner: In a 500-ml, 3-necked flask fitted with a reflux condenser, stirrer, thermometer, and gas inlet tube were placed 350 ml of benzene and 39.6 g (0.195 mole) of the disiloxane. Methylamine was passed in while the liquid was being stirred. After three hours, there was no further evidence of reaction. A positive pressure of methylamine was maintained with the aid of a balloon, and stirring was continued for two hours. After standing overnight the clear supernatant liquid gave a negative Beilstein test. The mixture was refluxed for three hours, and filtered. The amount of hydrochloride removed was 25.0 g (theoretical, 25.3 g) The benzene was distilled in a 1 x 30-cm packed column, and four fractions of the product were distilled:

1.	B p. 80-82°C at 44 mm	11.7 g
2.	B. p. 82°C at 44 mm	1.1 g
3.	B. p. 88°C at 15 mm	0.3 g
4.	B. p. 75°C at 3 mm	11.7 g
5.	Residue, pot at 200°C at 3 mm	4.9 g
		29.7 g

The neutral equivalent of Fraction **4** was **157.3** (theoretical for the eight-membered ring, **161.3**). Fractions **3** and **4** were combined and redistilled in the **1 x 30**-cm packed column. The following fractions were obtained.

1a.	B.p. 38°C at 1.5 mm	3.0 g
2a.	B.p. 38-40°C at 1.5 mm	3.0 g
3a.	Residue	4.0 g

The molecular weight of Fraction **2a** was **290**, as determined cryoscopically in cyclohexane. The theoretical value for an eight-membered ring is **322.7**. The elemental analysis and other data are listed in Table X. Identity as the eight-membered ring compound was not established.

The thermal stability of Fraction **2a** was determined by heating **0.1188** g in a **4.5**-ml evacuated, sealed glass tube at **450°C** for **1.5** hour. The amount of permanent gas remaining was **0.10** ml, or **0.84** ml per g. Thus the thermal stability is comparable to that of octamethylcyclotetrasiloxane, and less than that of several pure silazanes.

The reaction between methylamine and **1,5**-dichlorohexamethyltrisiloxane was carried out in the following manner. In a **500**-ml, 3-necked flask fitted with a stirrer, reflux condenser, gas inlet tube, and thermometer were placed **200** ml of benzene and **17.4** g (**0.063** mole) of the dichlorotrisiloxane. Methylamine was passed in slowly with stirring for **45** minutes while the temperature rose to **58°C**. Thereafter the mixture was stirred for two hours while a positive pressure of methylamine was maintained with the aid of a balloon. After the solution was refluxed for three hours, the supernatant liquid gave a negative Beilstein test. The hydrochloride (**8.1** g) was filtered off (theoretical, **8.4** g). The benzene was removed by distillation in a **1 x 30**-cm packed column. Considerable difficulty was experienced with boiling points that decreased as distillation progressed. Consequently all of the product was returned to the pot, and the entire amount was refluxed for two hours at atmospheric pressure. Then five fractions were obtained by distillation:

1. B.p. 87-159°C, atm. press.,   3.7 g
2. B.p. 159°C, atm. press.,   3.8 g
3. B.p. 81°C at 49 mm   1.1 g
4. B.p. 54°C at 3 mm   1.2 g
5. Residue, pot at 160°C at 3 mm   2.5 g

                                    12.3 g

Fraction **2** had a neutral equivalent of **301** (theoretical for a six-membered ring as in Figure **1 D, 235. 5**). The residue, Fraction **5,** was heated in an open tube to determine its fluid range. After starting to bubble gently at **170°C** the liquid temperature rose and eventually reached **400°C**. On cooling to **0°C** the material remained an oil.

Table X.   Physical and Chemical Data on the Compound Made from Methylamine and **1, 3**-Dichlorotetramethyldisiloxane

Analysis	Found	Theoretical[a]
Carbon, %	35. 58	37. 22
Hydrogen, %	8. 29	9. 37
Nitrogen, %	8. 80	8. 68
Silicon, %	30. 00	34. 81
Remainder, % (presumably oxygen)	17. 33	9. 92
Neutral equivalent	157	161. 4
Molecular weight (cryoscopic in cyclohexane)	290	322. 7

[a] $C_{10}H_{30}N_2O_2Si_4$,   Figure 1 C

I. Polymerization Through the Silicon-Hydrogen Bond

1. Discussion

The reaction of ammonia with silicon-hydrogen bonds offers a possible route to polymers containing silicon-nitrogen bonds. In published work, amines have been shown to react with silicon-hydrogen bonds in the presence of alkali metals.[20]

This reaction was therefore used in our attempts to make polymers. In order to prepare the starting material, methyldichlorosilane was treated with ammonia as follows, to prepare either cyclic compounds or linear polymers:

$$\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Cl-Si}} - Cl \ + \ NH_3 \ \longrightarrow \ \left[-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Si}} - \overset{H}{N} - \right]_x$$
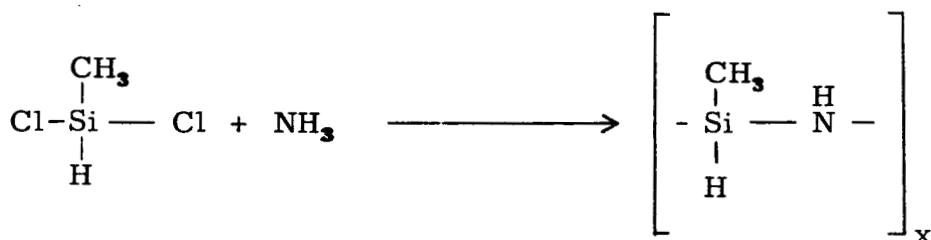
The product was expected to react as follows when the silicon-hydrogen bonds were treated with ammonia in the presence of potassium.

$$-\underset{\underset{|}{HN}}{\overset{\overset{CH_3}{|}}{Si}} - H \ + \ NH_3 \ \xrightarrow{\ K\ } \ \left[-\underset{\underset{|}{HN}}{\overset{\overset{CH_3}{|}}{Si}} - \overset{H}{N} - \underset{\underset{|}{HN}}{\overset{\overset{CH_3}{|}}{Si}} - \right]_x$$
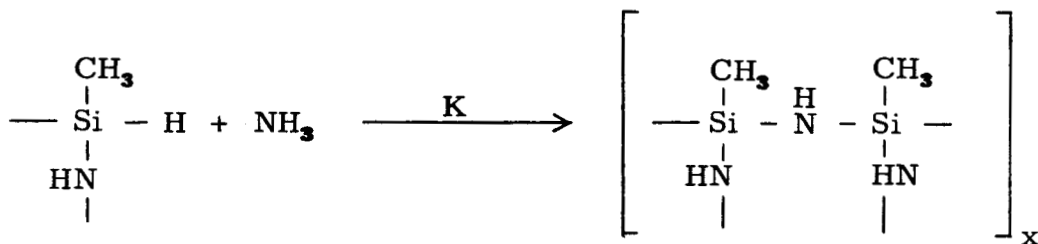
This reaction, if driven to completion, would form cross-linked polymers.

---

20. B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, Zhur. Obschei Khim. 27, 678 (1954); Chem. Abs. 49, 5272 (1955).

The product of the reaction of methyldichlorosilane with ammonia was largely polymeric. In two successive reactions, the second of which was done with exceptional care to exclude moisture, the neutral equivalents of the products were approximately **75**. Inasmuch as the theoretical neutral equivalent was **59** for $-SiHCH_3NH-$, it appears that some chain branching may have occurred, forming some trisilyl-substituted nitrogen atoms. Evidently cyclization was less of a problem than it has been in the previous reactions of dichlorosilanes with ammonia.

The polymeric product was a viscous liquid. When boiled in a test tube, it began to form a solid when the temperature of the melt reached **318°C**. The product was a foamed, white, tough, infusible solid. The gases evolved during the condensation were highly combustible. The condensation reaction may have occurred by one or both of these mechanisms:

```
    Me        Me        Me        Me
 - Si - N - Si - N - Si - N - Si - N -
    H   [H]  H   H  [H]  H   H   H
        |            |
        |            |                    ------->   CH4  or  H2
        |            |
    H  [Me] H   Me [H]  Me  H   Me
    N - Si - N - Si - N - Si - N - Si -
        H        H        H        H
```
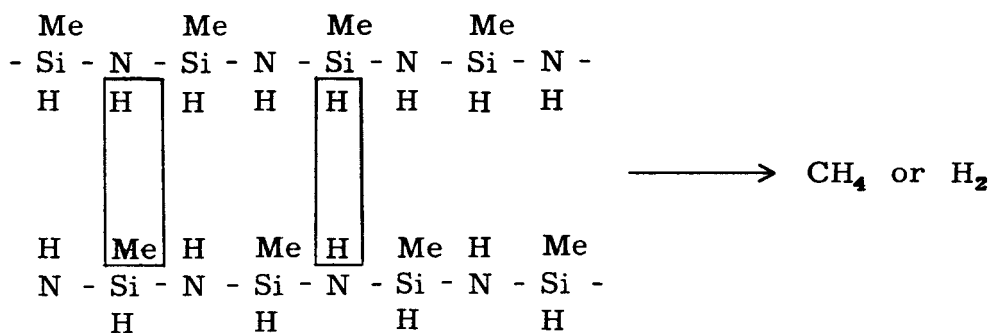
The liquid polymeric product gelled in several hours of exposure to air, but it remained clear and colorless. It could easily be made into a coating by spreading it in a thin film on aluminum and heating at **100-150°C**. The cured coatings resembled those made from hexaphenyl-cyclotrisilazane, but they were less stable. This is the lowest temperature at which the condensation polymerization of silazanes has been observed, and thus the reaction has considerable potential interest, especially for coatings that can be cured at moderate temperatures.

The cross-linking reaction with ammonia was relatively unsatisfactory because of the apparently low nitrogen content of the product and its intractable character. Although it has not been proved that cross-linking occurred through the silicon-nitrogen bonds, this is the most probable explanation. It will be difficult to show any utility for the reaction unless it can be conducted in a manner that will make it possible to manipulate the product. Cross-linking by amination of the silicon-hydrogen bonds will not be proved unless the product can be shown to have a high nitrogen content.

2. Experimental details

The first reaction of methyldichlorosilane with ammonia was modeled after the standard method of making hexamethylcyclotrisilazane. In a 1-liter, 3-necked flask fitted with reflux condenser, thermometer, stirrer, and gas-inlet tube were placed 600 ml of benzene and 115.1 g (1 mole) of methyldichlorosilane. Ammonia was passed in slowly for 1.25 hour. A positive pressure of ammonia was kept on the reaction for 3.75 hours by means of an inflated balloon. The solution was refluxed for three hours, and the hydrochloride was then filtered off, leaving a clear benzene solution which was negative to the Beilstein test. The benzene was distilled in a 1.2 x 30-cm column packed with small perforated stainless steel rectangles bent in the form of "C's". Some material (8.2 g) distilled at 126-160°C at 1.5 mm. The main product was 30 g of a cloudy viscous liquid which did not distill at 1 mm and at a pot temperature of 205°C and which had a neutral equivalent of 74. The neutral equivalent for

$$\begin{bmatrix} & H & \\ & | & H \\ - & Si - N & - \\ & | & \\ & CH_3 & \end{bmatrix}_x \quad \text{is 59.1.}$$
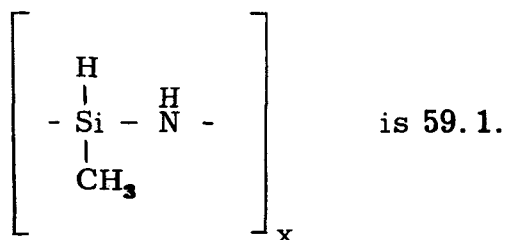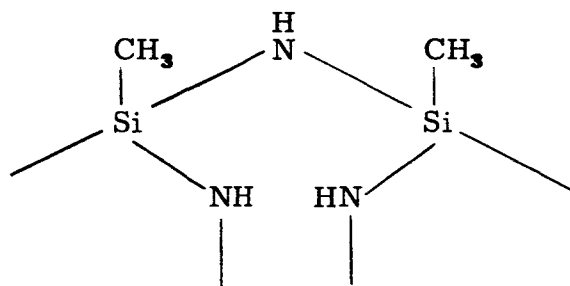
The second reaction of methyldichlorosilane with ammonia was run with more than the usual precautions to exclude moisture. In a 1-liter, 3-necked flask fitted with reflux condenser, stirrer, and gas-inlet tube were placed 600 ml of benzene and 115.1 g (1 mole) of recently distilled methyldichlorosilane. Liquid ammonia was placed in a 500-ml round-bottomed flask and sodium was added producing the dark blue color of dissolved sodium. Thereafter ammonia for the reaction distilled from the flask containing sodium, and the reaction was conducted in the manner just described for the first reaction. Before any solvent was removed from the reaction mixture, a sample of the clear supernatant liquid was taken to determine the neutral equivalent. The sample was evaporated in a tared beaker in an atmosphere of dry nitrogen, and the neutral equivalent of the residue was found to be 75. The benzene was removed from the product through a fractionating column. No volatile product was detected. The undistillable product remaining at 195°C at 3.5 mm pressure was a cloudy, white, viscous oil with a neutral equivalent of 83.

The methyl hydrogen silazane was dissolved in benzene and applied to aluminum in the form of thin coatings. One such coating was cured at 115°C for ten minutes to produce a colorless, transparent varnish-like film. When the panel was immersed in 10% hydrochloric acid, the acid began to dissolve the aluminum wherever it was not coated. After standing overnight the acid was exhausted, and the coating was largely but not entirely removed from the panel. Pieces of the coating were floating in the liquid. Evidently the coating was not sensitive to hydrolysis after curing at 115°C.

The coating failed in 20 minutes at 550°C in air, but it was still intact and effective against 20% hydrochloric acid after 40 minutes in air at 400°C. These experiments are being refined to determine the performance at temperatures between 400°C and 550°C. Failure on heating occurred by chalking rather than discoloration or flaking.

The attempt to cross-link the methyl hydrogen silazane was done in this manner. In a 100-ml round-bottom flask fitted with a dry-ice-cooled reflux condenser and magnetic stirrer was placed 5.9 g (0.1 mole) of the methyl hydrogen silazane obtained in the first reaction.

Liquid ammonia, 40 ml, was added, whereupon the silazane became quite hard. After considerable difficulty the silazane was broken away from the walls of the vessel with a spatula, and stirring became possible though not efficient. Potassium metal, 1.0 g (0.028 mole), was added to the ammonia solution in small amounts over a period of 1.25 hour. A blue color formed which remained during the entire reaction. After refluxing for six hours, the solution stood overnight while the ammonia was allowed to evaporate. The product was mixed with 40 ml of benzene and refluxed for two hours, but only part of the solid dissolved. After cooling, the benzene solution was centrifuged. The benzene was evaporated and a small amount of a cloudy white grease was obtained. The insoluble solid product was a mixture of a transparent, colorless, infusible polymer and some gray insoluble material that contained potassium. The clear insoluble polymer was separated and was reported to contain 8.5% nitrogen, but this report was probably inaccurate as explained in the next attempt. The theoretical nitrogen content is 42.8% for a cross-linked polymer having this repeating unit:

$$
\begin{array}{c}
\text{H} \\
\text{CH}_3 \quad \text{N} \quad \text{CH}_3 \\
| \quad\quad\quad | \\
\text{Si} \quad\quad \text{Si} \\
\quad \text{NH} \quad \text{HN} \\
\quad | \quad\quad | \\
\end{array}
$$

A second attempt to cross-link was made in the same manner as the first except that the silazane was placed on the wall of the reaction flask and cooled to hold it in place. The liquid ammonia was added by distillation from a flask of ammonia and sodium. After stirring was started, the silazane dissolved slowly and the reaction proceeded essentially as before. The clear insoluble polymer was reported to contain 7.5% nitrogen by the Dumas method. However, the Kjeldahl method of analysis showed a nitrogen content of 23.2%. The results are listed in Table XI.

Even if the reaction proceeded as expected, some means will have to be found of manipulating the product if it is to be useful. However, the silazane polymer made from methyldichlorosilane and ammonia merits further attention in connection with coatings.

Table XI. Elemental Compositions of Compounds Made from
Methyldichlorosilane

| | Found | | | Theoretical | |
	Compound A	Compound B	Compound C	Compound D	Compound E
Carbon, %	-	17.83		20.31	18.29
Hydrogen, %	-	6.02		8.52	6.91
Nitrogen, % (Dumas)	8.46	7.53	11.67	23.68	32.01
(Kjeldahl)		23.19			
Silicon, %	-	37.1		47.49	42.79
Total, %		84.14		100.00	100.00

A. Insoluble polymer obtained in first cross-linking reaction with potassium.

B. Insoluble polymer obtained in second cross-linking reaction with potassium.

C. Insoluble polymer obtained in thermal polymerization of Polymer D (below).

D. Cross-linked polymer obtained by these reactions:
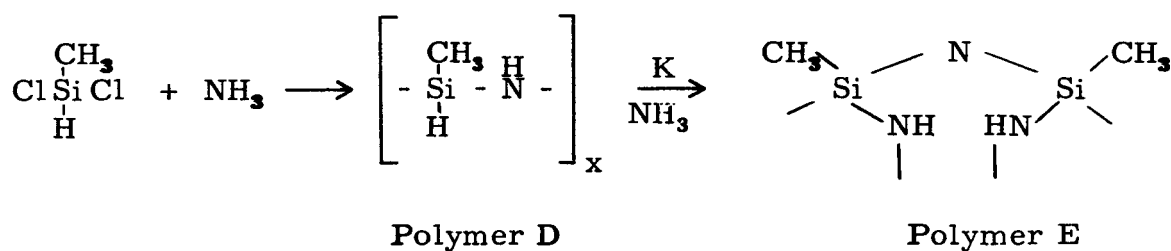
Polymer D   Polymer E

J. Reaction of Urea with Dimethyldichlorosilane

As one phase of the study of silicon-nitrogen polymers, we wished to determine whether Si-N polymers can be formed by the reaction of dimethyl-dichlorosilane with urea. Gilman[21] obtained an isocyanate when he treated urea with triphenylchlorosilane:

$$Ph_3SiCl + H_2N-CO-NH_2 \longrightarrow Ph_3SiNCO + NH_4Cl$$
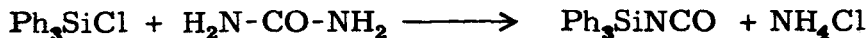
Hurkwitz[22] made a silicon derivative of acetamide by treating acetamide with triphenylchlorosilane and triethylamine in benzene.

$$CH_3CONH_2 + PH_3SiCl \xrightarrow{Et_3N} CH_3CONHSiPh_3$$
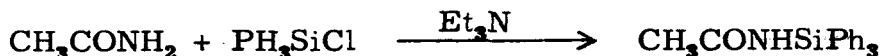
Our first attempt was a simple exploratory reaction. Urea, 1.0 g (0.016 mole), was refluxed and stirred for six hours at 71°C with 26.9 g (0.208 mole) of dimethyldichlorosilane. The urea changed from a freely stirring solid to a soft lump around the stirrer. The liquid was decanted, and the solid was washed with benzene. After drying, the solid product weighed 1.7 g. The theoretical yield of solid would have been 1.93 g if a polymer of the following composition had been formed:

$$\left[\begin{matrix} H & O & H & CH_3 \\ -N - C - N - Si - \\ & & & CH_3 \end{matrix} \right]_x$$
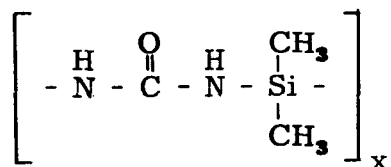
If the solid had been only ammonium chloride, the weight would have been 0.89 g. The product gave a positive Beilstein test, but that is not especially significant in view of the sensitivity of the test. The solid product fused partially, and decomposed when heated moderately on a spatula.

Evidently some reaction occurred between the urea and the halosilane, but it was not solely formation of either isocyanate or polymer. The experiment was inconclusive and the subject was set aside in favor of other reactions.

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21. H. Gilman, B. Hofferth, and H. W. Melvin, J. Am. Chem. Soc. 72, 3045 (1950).

22. M. J. Hurkwitz, E. Park, and P. L. de Benneville (to Rohm and Haas Company), U. S. Patent 2,876,234 (1959).

K. Attempts to Prepare Phenyl Silazanes with N-Methyl Groups

1. Discussion

The high thermal stability of hexaphenylcyclotrisilazane and nonamethylcyclotrisilazane suggested that a compound with both N-methyl and Si-phenyl substitution would have even greater stability. Accordingly the reaction of diphenyldichlorosilane with methylamine was studied. The products were diphenyldi(methylamino)silane, and a mixture of polymers.

Diphenyldi(methylamino)silane polymerized with evolution of methylamine on prolonged refluxing at atmospheric pressure. From the product was isolated a compound melting at 231°C, which was not purified and identified.

The polymer mixture from the reaction of diphenyldichlorosilane with methylamine polymerized further on heating above 200°C, with the evolution of gas. On continued heating, the material solidified, and the resulting solid was exceptionally stable and did not melt or decompose when heated on an aluminum panel even as the panel began to soften. Fibers could be drawn from the incompletely polymerized melt.

Additional work on this polymer appears to be justified because of its high thermal stability and high molecular weight.

2. Experimental details

Diphenyldichlorosilane, 253.2 g (1.0 mole), was dissolved in three liters of benzene in a 5-liter, 3-necked flask fitted with a stirrer, reflux condenser, thermometer, and gas-inlet tube. Methylamine was passed in above the surface of the solution for 3.5 hours as it was being stirred, and the temperature was kept below 30°C. The mixture was then refluxed for three hours and filtered. The product was distilled through a 1.2 x 30-cm packed fractionating column. The distillation data are in Table XII. Fractions 1-4 were undoubtedly diphenyldi(methylamino)silane,

H   Ph   H
CH$_3$N - Si - NCH$_3$,   which was first prepared by Larsson and Bjellerup,[23]
        Ph   who did not mention its melting point.

Table XII.   Distilled Product of Reaction Between Diphenyldichlorosilane
and Methylamine

Fraction	Boiling point, °C	Pressure, mm Hg	Weight, g	n_D^{25}	Melting point, °C	Neutral equiv.	Molecular weight[a] (cyclo-hexane)
1	132-136	0.5	26.5	1.5691	18.2		
2	134-136	0.5	24.7	1.5711	16.2		
3	137-138	0.5	23.8	1.5704	17.6		
4	135-138	0.5	32.7	1.5701	17.8	132	230
5	residue	0.5	37.2				

[a] Theory for diphenyldi(methylamino)silane; m.w. 242.39; neutral equivalent, 121.2.

23.   Erik Larsson and Lars Bjellerup, J. Am. Chem. Soc. 75, 995-997 (1953).

When the diphenyldi(methylamino)silane was refluxed for four hours, methylamine was evolved and the melt temperature reached 395°C. The product solidified on cooling. Recrystallization from a mixture of benzene and Skellysolve "B" produced a compound having a melting point of 231°C. Cyclization probably occurred, but more data are needed before a conclusion is attempted. Attempts to purify it further resulted in degradation, and continued work did not appear to be justified.

The undistillable product of the reaction between diphenyldichlorosilane and methylamine was a semicrystalline viscous mixture. It polymerized further when heated above 220°C with the evolution of gas, and on continued heating the decomposition temperature rose and reached a melt temperature of 455°C, whereupon the material solidified. The resulting solid did not melt or decompose when heated on an aluminum panel even as the panel began to soften.

Fibers could be made from the partially polymerized material when the melt temperature was 400-450°C, by touching the melt with a glass rod and withdrawing it quickly. The fibers, which were fairly flexible, softened in the range of 100-200°C but did not visibly decompose even near 500°C. They were not visibly affected by soaking in water. Ultraviolet light case-hardened the fiber but did not otherwise improve its properties. Gamma radiation, 3.2 megaroentgens, did not cause any obvious change.

L. Study of Nonamethylcyclotrisilazane and Its By-Products

1. Discussion

Nonamethylcyclotrisilazane was described in the preceding annual report.[1] When its thermal stability was compared with that of other silazanes it proved to be the most stable, as judged by the amount of gas produced on heating 1.5 hour at 450°C in a sealed evacuated glass tube. Because of its high thermal stability, several attempts were made to polymerize it or make polymers related to it.

The attempts to polymerize nonamethylcyclotrisilazane by heat did not produce polymers, but they did reemphasize its thermal stability. Heating nonamethylcyclotrisilazane in a sealed tube at 400°C for 456 hours reduced its melting point insignificantly. Similar treatment with potassium hydroxide added as a polymerization catalyst also caused little change. The results discussed below in Section III indicate that ammonium chloride or ammonium sulfate should be tried as catalysts.

An interesting by-product of the early syntheses of nonamethyl-cyclotrisilazane was a material containing end-amino groups.[1] We wished to determine whether the end-amino groups could be covered with trimethylsilyl groups by reacting them with trimethylchlorosilane. The by-product was thought to be 1,3-bis(methylamino)-pentamethyldisilazane; and, if so, the reaction was expected to proceed in this manner:

$$
\begin{array}{c}
\text{Me Me Me Me Me} \\
\text{HN - Si - N - Si - NH} \\
\text{Me} \qquad \text{Me}
\end{array}
+ 2\ \text{ClSi(Me)}_3 \longrightarrow
\begin{array}{c}
\text{Me Me Me Me Me Me Me} \\
\text{MeSi - N - Si - N - Si - N - SiMe} \\
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me}
\end{array}
$$

1,3-bis(methylamino)pentamethyldi-   tridecamethyltetrasilazane
    silazane
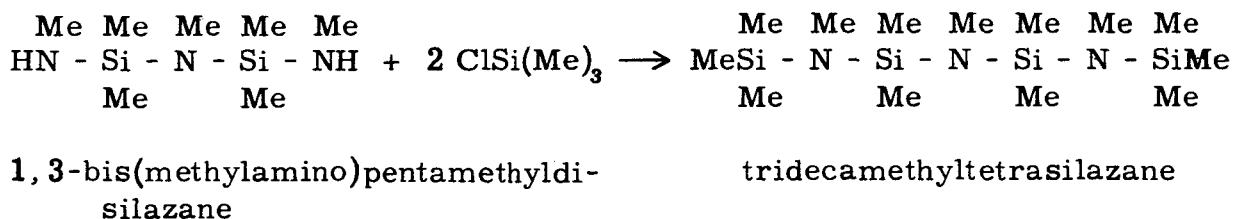
Tridecamethyltetrasilazane would be interesting because of its linearity, its lack of N-hydrogen groups, and its high degree of steric hindrance. The first attempted synthesis was not successful, probably because the starting material was not the desired compound. The neutral equivalent of the product was 342, whereas the molecular weight of tridecamethyltetrasilazane

is **349.8,** and the expected neutral equivalent after hydrolysis would be **116.6.** The similarity between the observed neutral equivalent and the molecular weight was probably coincidental. It would be quite interesting however to prepare a fully methylated linear silazane to determine its properties. Resonance would be reduced in the linear compound, as compared to the cyclic nonamethylcyclotrisilazane and hence the thermal stability would be less.

The distillation residue was another interesting by-product of the reaction of dimethyldichlorosilane with methylamine. As described below in Section IV. D. a still residue from an early reaction polymerized to an elastomer on standing for ten months in a desiccator.

2. Experimental details

We hoped to obtain nonamethylcyclotrisilazane and its two by-products from a single "series reaction," in which an excess of each reactant was added successively. However, this was not the method of synthesis used to prepare the by-product initially; and the by-products obtained in the "series" reaction were not satisfactory, although nonamethylcyclotrisilazane was obtained as expected.

The series reaction to produce nonamethylcyclotrisilazane was conducted in the following manner. In a **5-liter, 3-**necked flask fitted with a stirrer, reflux condenser, thermometer, and gas inlet tube were placed **250** g **(1.93** moles) of dimethyldichlorosilane and **1750** ml of benzene. Methylamine was passed in for three hours through a gas inlet tube, which extended to an inch above the surface of the liquid. At that time no further reaction could be detected. During this period, **400** ml of benzene was added to facilitate stirring, and the temperature rose to **80°C.** The mixture was then refluxed for three hours. The solution was filtered, the amine hydrochloride was discarded, and the clear benzene solution was returned to the flask. Dimethyldichlorosilane, **80** g **(0.62** mole), was added dropwise with stirring, and the solution was again refluxed for three hours. Methylamine was passed over the

stirred solution as before for 1.5 hours until no reaction was detectable by temperature rise; the mixture was refluxed for three hours, and then it was filtered to remove the salt. The addition of dimethyldichlorosilane, 80 g (0.62 mole), and of methylamine were repeated as before. After a final filtration, the benzene was removed by distillation, and the product was distilled through a 1.2 x 30-cm column filled with 4 x 6-mm perforated rectangles of stainless steel bent in the form of C's. The distillation data are in Table XIII.

Fractions 6, 7, and 8 of Table XIII were crude nonamethylcyclo-trisilazane amounting to 35% of the theoretical yield. By recrystallization 21% of the theoretical yield of product, melting at 35-36°C, was obtained. Fraction 2 was believed to be the compound having end-amino groups, MeNH-SiMe$_2$-NMe-SiMe$_2$-NHMe, because of its boiling point. The original compound boiled at 79-80°C at 13 mm.[1]

Fraction 2 (16.4 g, 0.08 mole, assumed) was added dropwise with stirring to 180.6 g (1.76 mole) of trimethylchlorosilane in one liter of benzene. The addition required ten minutes and the resulting mixture was refluxed for three hours. The product was eventually distilled in a 1.2 x 30-cm packed fractionating column over a wide boiling range: from 88°C at 30 mm to 169°C at 0.3 mm. The neutral equivalent of the total product was 342, whereas the theoretical neutral equivalent for hydrolyzed tridecamethyltetrasilazane is 116.6. Because of the possibility that contamination by moisture caused the high neutral equivalent, the experiment was inconclusive. Time was not allotted to pursue the problem further.

In the thermal stability experiments, 0.35 g of nonamethylcyclo-trisilazane was sealed in a 5-ml evacuated Pyrex tube and heated at 400°C for 456 hours. The melting point was taken periodically by immersing the tube in a water bath. The melting point changed from the initial value of 35.4°C to 32.0-32.9°C after 456 hours.

In a similar experiment, 0.04 g of potassium hydroxide was added. After 141 hours, the melting point was 28-29°C.

Table XIII. Distillation of Product from Reaction of Dimethyldichlorosilane
and Methylamine

Fraction	Weight, g	Boiling point, °C	Pressure, mm
1	8.3	49-59	6
2	21.9	59-60	6
3	11.3	60-62	6
4	14.3	62-65	6
5	10.7	44-54	1
6	43.4	54-60	1
7	32.3	60-63	1
8	21.4	63-67	1
9	2.8	67-78	1
Residue	19.9		
	186.3		

III. METHODS OF POLYMERIZING SILAZANES

Silazanes are easily prepared by the reaction of amines with chlorosilanes, but cyclization usually defeats attempts to form high polymers when the amine and the silane are each capable of reacting only twice. Although three methods have succeeded in producing polymers, some having molecular weights of several thousand, molecular weight still remains one of the primary problems in producing silazanes with adequate strength. Although considerable effort has been made to increase molecular weights, the attempts have by no means been exhaustive, and it is possible that each of the three methods could be developed to produce significantly higher molecular weights. The three methods are thermal polymerization of silazanes, amine exchange with polyfunctional amines, and the addition of a trifunctional silane to the amine-dichlorosilane reaction mixture.

A. The Amine Exchange Reaction

1. Discussion

Silylamines exchange with amines in the presence of acid catalysts:

$$\equiv Si - \overset{H}{N} - R \ + \ R'NH_2 \ \underset{\longrightarrow}{\longleftarrow} \ \equiv Si - \overset{H}{N}R' \ + \ RNH_2$$
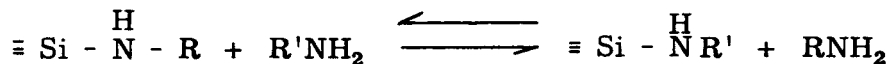
If the attacking amine is less volatile than the amine being displaced, the reaction can be driven to the right by distillation of the more volatile amine. An excellent review of past work on this subject is available.[24] Fessenden emphasized the subject in a private communication.[3] Past work dealt mainly with synthesis of silylamines of low molecular weight.

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24. R. Fessenden and J. S. Fessenden, Chem. Rev. 61, 361-388 (1961).

Ammonium salts and trimethylchlorosilane have been recommended as catalysts. We have tried ammonium sulfate, ammonium chloride, and dimethyldichlorosilane, and all three were partially successful. The ammonium sulfate did not go into solution, and it appeared to be decomposed at temperatures over 200°C. In one reaction at 250°C the odor of hydrogen sulfide was detected. In others the ammonium sulfate became covered with solid insoluble matter that deactivated it. The dimethyldichlorosilane was converted quickly to a silylamine plus ammonium chloride or amine hydrochloride. Ammonium chloride apparently performed as well as the others, but at present there is little reason for choosing any one catalyst over the others. There seems to be much room for improvement in the catalyst.

When benzene was tried as a solvent for amine exchange, no reaction occurred. Pyridine and quinoline were fairly effective as reaction solvents. However, it appears that the main factor in producing high molecular weights is high temperature and that solvent is not beneficial. All of the polymers that have been made by amine exchange are red-brown with varying degrees of hardness. Silazanes with phenyl substituents were not successfully polymerized.

A product from the reaction of octamethylcyclotetrasilazane, ethylenediamine, and ammonium chloride appeared to have the highest molecular weight of the products that were made, as it was the toughest and highest melting. It was not sufficiently soluble in benzene for its molecular weight to be determined, although it was swollen by benzene or xylene to give an elastomer. Heating in air at 400°C produced a relatively tough elastomer.

Piperazine and n-butylamine, both of which are difunctional, did not polymerize successfully with hexamethylcyclotrisilazane. Reactions occurred, but high polymers were not produced.

In spite of the low molecular weights observed, fibers could be drawn from several of the polymers.

The mechanism of the reaction is said to involve the formation of a protonated silylamine, $- \overset{\displaystyle |}{\underset{\displaystyle |}{Si}} - \overset{\displaystyle H}{\underset{\displaystyle H^+}{N}} - \overset{\displaystyle |}{\underset{\displaystyle |}{Si}} -,$ as an intermediate, followed by nucleophilic attack by the entering amine.[24] If such is the case, it would seem possible to form polymers of either of these types:

or
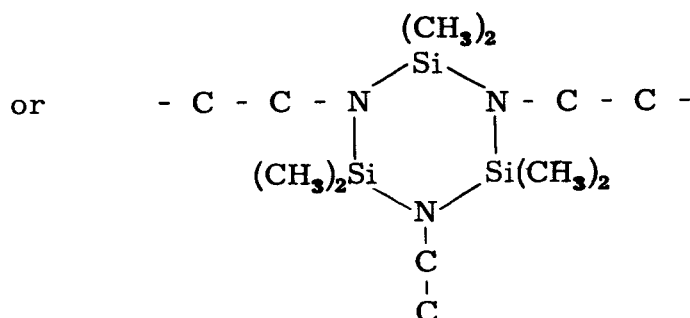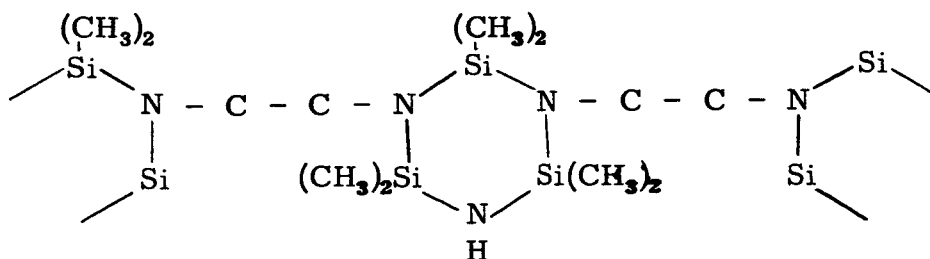
However, steric hindrance is a factor, and the ring is evidently not stable, because hexaphenylcyclotrisilazane was disrupted by aniline to form dianilinosilane rather than a cyclic silazane.[23] Probably the silazanes are disrupted sufficiently to lose their original ring structure and form chains of silicon-nitrogen bonds separated by ethylene units in this manner:
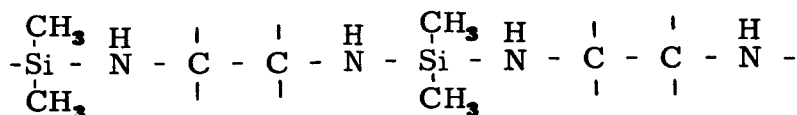
Branching is also possible in this manner:

$$(CH_3)_2Si - \overset{\text{H}}{\underset{|}{N}} - C - C - \overset{\text{H}}{N} -$$

$$\underset{\overset{|}{CH_3}}{\overset{CH_3}{\underset{|}{-Si}}} - \overset{\text{H}}{N} - C - C - \underset{|}{N}$$

$$(CH_3)_2Si - \underset{\text{H}}{N} - C - C - \underset{\text{H}}{N} -$$
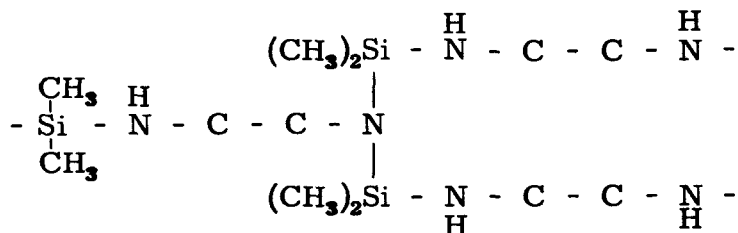
It is evident from any view of the possible structures that the silazane-diamine reaction is capable of almost endless variations when the diamine has four replaceable hydrogens. However, when piperazine is the diamine, a linear structure is unavoidable, as long as the cyclic structure of the piperazine is not destroyed.

$$\underset{\overset{|}{CH_3}}{\overset{CH_3}{\underset{|}{-Si}}} - N \underset{C-C}{\overset{C-C}{<\quad>}} N - \underset{\overset{|}{CH_3}}{\overset{CH_3}{\underset{|}{Si}}} - N \underset{C-C}{\overset{C-C}{<\quad>}} N -$$
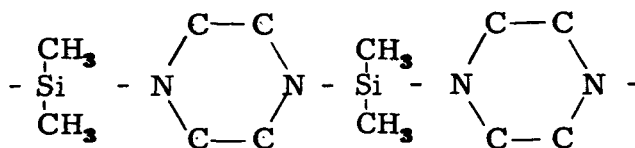
Piperazine reacted more slowly than ethylenediamine.

2. Experimental details

The amine exchange reactions described below are summarized in Table XIV. Analytical results on several selected products of the amine-exchange reaction are reported in Table XV. Some of the molecular weights were estimated cryoscopically in benzene, and some were estimated by vapor osmometry. The latter method is believed more accurate for molecular weights above several hundred.

Table XIV. Amine-Silazane Exchange Reactions

Experiment no.	Silazane	Amine	Catalyst	Reaction time, hr	Final temp., °C	Final pressure, mm Hg	Molecular weight of product	Appearance of product
2483-129	Oc	En	$(NH_4)_2SO_4$	8	100	1.0	1800[b]	yellow grease
2483-133-1	HexMe	En	$(NH_4)_2SO_4$	6.5	140	2.0	2700[b]	yellow grease
2483-143	Oc	En	$(NH_4)_2SO_4$	13.5	180	0.3	3300[a]	red-brown solid
2483-137	HexMe	Pip	$(NH_4)_2SO_4$	4.5	148	0.5	400[a]	red-brown oil
2614-17	HexMe	Bu	$(NH_4)_2SO_4$	6.0	195	3.0	800[b]	red-brown oil
2483-157	Oc	En	Me_2SiCl_2	15.5	200	0.6	>3,000[b]	yellow wax
2483-159	HexPh	En	$(NH_4)_2SO_4$	23.0	240	0.1	560[b]	black vitreous solid
2614-29	HexPh + HexMe	-	$(NH_4)_2SO_4$	27.0	230	1.0	1100[a]	red-brown, tacky semi-solid
2614-31	Nona	En	NH_4Cl	16.5	120	0.1	d	red-brown, soft solid, hygroscopic
2614-39	MePh	En	NH_4Cl	9.0	210	0.1	2300[a]	red-brown, soft solid
2614-45	Octa	En[c]	NH_4Cl	25.0	140	25	2400[b]	red-brown, soft solid
2378-143-1	Octa	En	NH_4Cl	12.5	175	0.2	d	red-brown, tough solid[e]
2614-63	Octa	En[f]	NH_4Cl	18.0	232	atm	>3000	red-brown, grease

[a] Estimated by vapor osmometry.

[b] Estimated cryoscopically in benzene.

[c] Carried out in pyridine solvent until the temperature was finally raised to drive the reaction further.

[d] Only partially soluble; accordingly molecular weight has not been determined.

[e] The toughest yet made; could be molded by heating.

[f] Carried out in quinoline.

Oc = octamethylcyclotetrasilazane.
HexMe = hexamethylcyclotrisilazane.
HexPh = hexaphenylcyclotrisilazane.
En = ethylenediamine.
Pip = piperazine.
Bu = butylamine.

Table XV. Character and Elemental Compositions of Several Polymers Made by Amine Exchange

Analysis	Found Experiment 2483-				Calculated			
	129	133	143	137	Oc or Hex[a]	En-reacted[b]	En-reacted[c]	Pip-reacted[d]
Carbon, %	43.28	36.59	39.52	43.75	32.83	41.80	41.33	50.65
Hydrogen, %	9.84	8.86	8.86	9.76	9.64	9.36	10.41	9.92
Nitrogen, %	16.44	17.21	14.80	17.00	19.14	16.25	24.10	19.69
Silicon, %	30.30	32.90	31.70	26.00	38.39	32.59	24.16	19.74
Remainder, % (presumably oxygen)	0.14	4.44	5.12	3.49				
Neutral equivalent (hydrolyzed)	85	92			73.2	86.2	58.1	71.14

a Theoretical for octamethylcyclotetrasilazane or hexamethylcyclotrisilazane, unreacted, $(C_2H_7NSi)_n$.
b Theoretical for octamethylcyclotetrasilazane or hexamethylcyclotrisilazane, with ammonia completely replaced by ethylenediamine in a cyclic silazane structure, $(C_3H_8NSi)_n$.
c Theoretical for octamethylcyclotetrasilazane or hexamethylcyclotrisilazane with ammonia completely replaced by ethylenediamine in a linear structure, $(C_4H_{12}N_2Si)_n$.
d Theoretical for octamethylcyclotetrasilazane and hexamethylcyclotrisilazane with ammonia completely replaced by piperazine in a linear structure, $(C_8H_{14}N_2Si)_n$.

a. Reaction of octamethylcyclotetrasilazane with ethylenediamine
   in solvent

In a 500-ml, 3-necked flask fitted with a magnetic stirrer, reflux condenser, and thermometer were placed 75 g (0. 256 mole) of octamethyl-cyclotetrasilazane (m. p. 95-97°C), 250 ml of benzene, and 15. 3 g (0. 256 mole) of ethylenediamine. Ammonium sulfate, 1. 5 g (0. 011 mole), was added with stirring. The ammonium sulfate had been dried previously in a desiccator over phosphorous pentoxide. There was a rapid evolution of gas at first, but it subsided quickly. The mixture was then refluxed for ten hours. During this time there was slow evolution of gas, and the ammonium sulfate became lumpy. At the end of the ten-hour period the solution was decanted from the ammonium sulfate, and the benzene was removed by distillation, the final pot temperature being 160°C. On cooling, the undistilled portion crystallized, and the melting point was found to be 85-88°C. Obviously, the reaction had not proceeded far. The catalyst had been deactivated by polymerization on its surface.

b. Reaction of octamethylcyclotetrasilazane with ethylenediamine
   (1:2 ratio) without solvent, Experiment 2483-129

In a 100-ml, 3-necked flask fitted with a thermometer, a reflux condenser, and magnetic stirrer were placed 25. 2 g (0. 086 mole) of octamethylcyclotetrasilazane and 5. 1 g (0. 086 mole) of ethylenediamine. The mixture was heated to make it homogeneous. Dry ammonium sulfate, 0. 5 g (0. 0038 mole), was added when the temperature was about 100°C and violent boiling resulted. The reaction subsided in a few minutes. Heating and stirring were continued for three hours, and ammonia was liberated throughout this entire period. The solution was cloudy, and it became progressively more viscous. An additional quantity of ethylene-diamine, 5. 1 g (0. 086 mole), was added, and heating was continued at 120°C for five hours. On cooling no crystals appeared. About two-thirds of the product was dissolved in xylene and centrifuged to remove the ammonium sulfate. The other third, 7. 7 g, was stored in case of future need. The xylene was removed by distillation, the final pot temperature being 100°C at 1 mm pressure. The yield of the centrifuged portion was 13. 9 g, and the total yield was 21. 6 g. It was a heavy grease. If each ammonia unit had been replaced by half of an ethylenediamine molecule, the yield would have been 29. 7 g. Evidently more than ammonia was lost during the reaction.

The neutral equivalent of the product (hydrolyzed) was **85**, whereas the theoretical value, if each ammonia unit had been replaced by half of an ethylenediamine molecule, would have been **86**. The neutral equivalent (hydrolyzed) of octamethylcyclotetrasilazane is **73**. The molecular weight was determined cryoscopically in benzene to be **1800** (the polymer was not readily soluble in cyclohexane). However, this figure should be regarded as approximate, because the amount of freezing point lowering was small, and a trace of insoluble matter was present. The polymer performed in a manner very similar to ethylenediamine silazane when cured by heating in air on a metal panel.

c. Reaction of hexamethylcyclotrisilazane with ethylenediamine (1:1 ratio) without solvent, Experiment 2483-133

In a **50**-ml, **3**-necked flask fitted with a thermometer, reflux condenser, and magnetic stirrer were placed **23.8** g (**0.108** mole) of hexamethylcyclotrisilazane, **1.62** g (**0.027** mole) of ethylenediamine, and **0.4** g (**0.003** mole) of ammonium sulfate. The mixture was heated to **110°C** and the evolution of ammonia was rapid. After **30** minutes, **1.62** g (**0.027** mole) of ethylenediamine was added, and the rate of ammonia evolution was increased slightly. After another **30**-minute interval the addition of ethylenediamine was repeated, whereupon the evolution of ammonia became unexplainably violent, and an estimated **3-5** ml of reactants was lost. The reaction subsided, and **30** minutes later the fourth addition of ethylenediamine was made with only a small amount of foaming. The mole ratio of ethylenediamine to hexamethylcyclotrisilazane at this time was **1:1**. After heating for an additional six hours at **110°C**, the entire product was refined by dissolving the xylene and centrifuging as described above in Section II. B. 2. for octamethylcyclotetrasilazane. The yield was **14.5** g. The neutral equivalent was **92**. This figure is higher than any that can be derived by simple stoichiometry, and so some foreign matter, possibly moisture, must have entered the reaction. The product was a grease, more viscous than the one derived from octamethylcyclotetrasilazane. The molecular weight was estimated cryoscopically, in benzene, to be **2700**. A sample of the grease placed on a glass slide and left exposed for a week in the laboratory became slightly more gummy. There was some hygroscopicity in the sample as evidenced by the formation of microscopic drops on the surface. However, that condition did not progress below the surface. The product performed in the manner of ethylenediamine silazane when cured by heating in air.

d. **Prolonged reaction of octamethylcyclotetrasilazane with ethylenediamine (1:2 ratio) without solvent, Experiment 2483-143**

In a 50-ml, 3-necked flask fitted with a reflux condenser, thermometer, and magnetic stirrer were placed 14. 0 g (0. 048 mole) of octamethylcyclotetrasilazane. The crystals were heated to melting and 0. 2 g (0. 0015 mole) of ammonium sulfate was added. With the mixture at 74°C, 5. 7 g (0. 096 mole) of ethylenediamine was added. There was a rapid evolution of ammonia. The solution was heated and stirred for ten hours at 110°C and then the temperature was raised to 180°C for 30 minutes. Then 0. 3 g (0. 0023 mole) of ammonium sulfate was added, and the mixture was heated two hours at 170°C. Then the sample was heated for one hour at 175°C at 0. 45 mm pressure. On cooling the mass solidified. It was dissolved in hot xylene and centrifuged. The xylene was removed by distillation. The product was very viscous at 180°C at 0. 3 mm pressure. On cooling it became a relatively hard brittle red-brown solid that could be dented with a fingernail and broken fairly easily with the fingers. When heated, the solid softened at 143°C and flowed at 168°C. Its molecular weight was estimated by vapor osmometry to be 3300. Its thermal stability was relatively poor, as judged by the comparison method previously described.[1] However, unstable impurities may have been responsible for the observed 38. 2 ml of gas produced per gram of polymer when a sample was heated in a sealed evacuated tube for 1. 5 hours at 450°C. A small piece dissolved slowly in boiling hydrochloric acid. The laboratory air caused microscopic droplets to form on the surface but no other visible change occurred immediately. A thin film when cured by heating in air behaved like ethylenediamine silazane, but the product appeared to be slightly tougher than cured ethylenediamine silazane when scraped with a knife.

e. **Reaction of hexamethylcyclotrisilazane with piperazine (1:2 ratio) without solvent, Experiment 2483-137**

In a 100-ml, 3-necked flask fitted with a thermometer, condenser, and magnetic stirrer were placed 15. 14 g (0. 069 mole) of hexamethylcyclotrisilazane, 5 g (0. 069 mole) of piperazine, and 0. 3 g (0. 0023 mole) of ammonium sulfate. The mixture was heated, and there was no evidence of gas production until the temperature reached 90°C. The temperature was

held at 140°C for 30 minutes, and ammonia was evolved slowly. An additional quantity, 5 g (0.069 mole), of piperazine was added, and heating was continued at 160°C for three hours. The mixture was then heated under reduced pressure until the pot temperature reached 160°C at 0.5 mm pressure, and those conditions were maintained for about one hour. The product was partially dissolved in xylene and centrifuged. Approximately 5% was insoluble in xylene and was removed at this point. The xylene was removed at reduced pressure, the final pot conditions being 148°C at 0.5 mm pressure. The product was a red-brown oil that would barely flow at room temperature. Its molecular weight was estimated by vapor osmometry to be 400.

> f. Reaction of hexamethylcyclotrisilazane with n-butylamine (1:3 ratio) without solvent, Experiment 2614-17

In a 100-ml, 3-necked flask fitted with magnetic stirrer, reflux condenser, and thermometer were placed 25.0 g (0.114 mole) of hexamethyl-cyclotrisilazane, 25.0 g (0.342 mole) of n-butylamine, and 1.5 g (0.011 mole) of dry ammonium sulfate. Heating was started, and evolution of gas started when the temperature reached 45°C. The temperature was raised slowly to 180°C and held there for five hours. At that temperature the solution turned black. After heating an additional hour at 200°C the product was distilled. The data on the fractions are shown in Table XVI.

The distillation residue was dissolved in 60 ml of benzene and clarified by centrifugation. The benzene was distilled, with the final conditions of the pot being 195°C at 6 mm. The liquid in the pot was very fluid at 195°C at 6 mm. When a small portion of this liquid was distilled in a small distillation flask, the main portion boiled at 320-375°C. This fraction was fluid at -50°C when cooled in a dry ice-acetone bath.

The neutral equivalent of Fraction III (hydrolyzed) was 175, whereas the theoretical value if all of the ammonia had been replaced would have been 129.3. The molecular weight was determined cryoscopically in benzene to be 800. The polymer was not readily soluble in cyclohexane.

Table XVI. Fractional Distillation of Product of n-Butylamine Exchange Reaction
Experiment 2614-17

Fraction no.	Vapor temperature, °C	Pressure, mm, Hg	Pot temperature, °C	Weight, g	Remarks
I	79-159	44		7.6	some solid and liquid
II	129-140	6		17.4	brown colored liquid
III		3	195	6.2	no distillation

Molecular weight of III, 800; Neutral equivalent, 175.

Theoretical neutral equivalent, 129.3, for
$$\left[\begin{array}{c} CH_3 \\ -Si - N - C_4H_9 \\ CH_3 \end{array} \right]_x$$
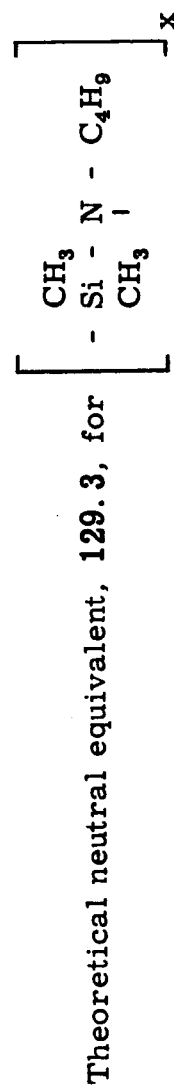
g. Reaction of octamethylcyclotetrasilazane with ethylenediamine (1:3 ratio) without solvent, Experiment 2483-157

In a 100-ml, 3-necked flask fitted with stirrer, reflux condenser, and thermometer were placed 20. 0 g (0. 067 mole) of octamethylcyclotetra-silazane and 12. 2 g (0. 203 mole) of ethylenediamine. The mixture was heated to 65°C to melt it and 0. 7 g (0. 006 mole) of dimethyldichlorosilane was added slowly. Heavy white smoke appeared with a small amount of gas evolution. The temperature was raised to 110°C and held there for six hours. The reaction mixture did not crystallize on cooling. Another 0. 7 g (0. 006 mole) of dimethyldichlorosilazane was added slowly. Heavy smoking occurred, and two layers formed. The reaction was heated for six hours at 180°C, and the product became viscous during this time. The temperature was raised to 200°C, the pressure was reduced to 0. 6 mm, and these conditions were maintained for 2. 5 hours. The total heating time was 15. 5 hours. The product was dissolved in xylene and centrifuged. The xylene was distilled with the final conditions in the pot being 120°C at 0. 5 mm. The yield was 22. 4 g of a waxy solid. The molecular weight was estimated cryoscopically in benzene to be above 3000.

h. Reaction of hexaphenylcyclotrisilazane with ethylenediamine (1:2 ratio) without solvent, Experiment 2483-159

In a 100-ml, 3-necked flask fitted with a stirrer, reflux condenser, and thermometer were placed 20 g (0. 0338 mole) of hexaphenylcyclotri-silazane, 4. 04 g (0. 0676 mole) of ethylenediamine, and 0. 4 g (0. 003 mole) of ammonium sulfate. The complex series of additions described below demonstrates that considerable effort was made to intensify the reaction conditions and force polymerization. The final prolonged heating at 200-240°C at 0. 1 mm pressure was an attempt to permit small ethylene-diamine-substituted molecules to condense by elimination of ethylenediamine. Evidently ammonia was replaced by ethylenediamine, but polymerization did not occur.

After the reactants were mixed, the temperature was raised to 120°C and held there for two hours. Inasmuch as some refluxing occurred, all of the ethylenediamine evidently had not reacted. The temperature was increased to 145°C for one hour; and then the red-orange solution was cooled to 120°C, and 0. 04 g (0. 003 mole) of dry ammonium sulfate was added. There was evolution of gas as the temperature was increased slowly to 230°C over a period of 1. 5 hours. The reaction was cooled to

120°C, and 4. 04 g (0. 0676 mole) of ethylenediamine was added slowly. After one hour of heating at 180°C, another 4. 04 g (0. 0676 mole) of ethylenediamine and 0. 4 g (0. 003 mole) of ammonium sulfate were added, and the reaction mixture was heated at 158°C for one hour. After the addition of another 0. 4 g (0. 003 mole) of ammonium sulfate, the reaction mixture was heated at 165°C for seven hours, and more gas was evolved. After being heated for 8. 5 hours at 200-220°C at 0. 1 mm, the product was very viscous. The temperature was raised to 240°C at 0. 1 mm and held there for two hours. The product was dissolved in xylene and centrifuged with about 10% of the total remaining undissolved. The xylene was distilled, with the final conditions in the pot being 275°C at 0. 1 mm. On cooling to 160°C, the product could be pulled into long brittle fibers. The yield was 19. 0 g of a black, shiny, brittle solid. The molecular weight was estimated cryoscopically in benzene to be 560.

i. Hexaphenylcyclotrisilazane and hexamethylcyclotrisilazane, Experiment 2614-29

In a 50-ml, 3-necked flask fitted with a thermometer, reflux condenser, and stirrer were placed 8. 8 g (0. 04 mole) of hexamethyl-cyclotrisilazane, 8. 8 g (0. 016 mole) of hexaphenylcyclotrisilazane, and 0. 3 g (0. 002 mole) of ammonium sulfate. The mass was heated and stirred at 200-230°C for seven hours and from 250-275°C for six hours. An additional 0. 3 g of ammonium sulfate was added, and the mass was heated at 270-290°C for four hours and at 320°C for one hour. Because there had been relatively little increase in viscosity, 0. 3 g of ammonium chloride was added to determine whether it would cause faster polymeri-zation. There was no detectable improvement. The mixture was heated at 320°C for six hours and at 230°C at 1 mm pressure for three hours. The mixture was then dissolved in xylene and centrifuged. The xylene was removed by distillation at low pressure. The product, a viscous, sticky, red-brown grease, weighed 10. 2 g. Evidently part of the reactants were lost by distillation. The molecular weight was estimated by vapor osmometry to be 1100.

When fractionation of this polymer was attempted by partially dissolving it in hexane, crystals were obtained. These proved to be hexaphenylcyclotrisilazane. Consequently, the phenyl compound was only slightly changed by the prolonged heating with ammonium sulfate and hexamethylcyclotrisilazane.

j. Nonamethylcyclotrisilazane and ethylenediamine, Experiment 2614-31

In a 100-ml, 3-necked flask fitted with a stirrer, reflux condenser, and thermometer were placed 10.5 g (0.04 mole) of nonamethylcyclotrisilazane, 7.2 g (0.12 mole) of ethylenediamine, and 0.2 g (0.0037 mole) of NH$_4$Cl. The mixture was heated and stirred at gradually increasing temperatures from 100-165°C for 14.5 hours. Then it was heated at 115-120°C at 0.1 mm pressure for two hours. At this point the product was a yellow grease. It was dissolved in xylene and centrifuged. The product was a soft, red-brown solid that was not completely soluble in cold benzene. On standing in the air, small droplets formed on the surface of the solid indicating hygroscopicity, and the solid deteriorated in two days.

k. Methylphenylsilazane and ethylenediamine, Experiment 2614-39

In a 50-ml, 3-necked flask fitted with a thermometer, stirrer, and reflux condenser were placed 4.3 g (0.072 mole) of ethylenediamine, 0.2 g (0.0037 mole) of ammonium chloride, and 10.0 g (0.024 mole) of mixed methylphenylsilazanes. The mixed methylphenylsilazanes were prepared by a reaction described previously.[1] The mixture was stirred one hour at 125°C, and 0.2 g (0.0037 mole) of ammonium chloride was added. Stirring was continued at 240-260°C for five hours, at 185°C at 0.05 mm pressure for one hour, and at 210°C at 0.1 mm pressure for two hours. The resulting red-brown viscous liquid was dissolved in xylene and centrifuged. The xylene was removed by distillation at reduced pressure to yield 7.2 g of a red-brown soft solid. The molecular weight was estimated by vapor osmometry to be 2300.

l. Octamethylcyclotetrasilazane and ethylenediamine in pyridine, Experiment 2614-45

In a 100-ml, 3-necked flask were placed 10 g (0.034 mole) of octamethylcyclotetrasilazane, 3.8 g (0.063 mole) of ethylenediamine, 0.2 g (0.0037 mole) of ammonium chloride, and 40 ml of pyridine that had previously been refluxed with phthalic anhydride, distilled, refluxed with potassium hydroxide, and distilled again. The solution was refluxed for three hours at 115°C. There was considerable evolution of ammonia. Ammonium chloride, 0.2 g, was added and refluxing was continued for eight hours. Another 0.2 g of ammonium chloride was added and refluxing

was continued for **14** hours. The pyridine was distilled off, the final conditions of the residue being **140°C** at **25** mm. The product was dissolved in xylene, centrifuged, and recovered by distillation of the xylene at reduced pressure. The product was **8.1** g of red-brown soft solid. The molecular weight was estimated cryoscopically in benzene to be **2400**.

m. Octamethylcyclotetrasilazane and ethylenediamine
without solvent, Experiment **2378-143-1**

In a **100-ml**, **3-necked** flask fitted with a stirrer, reflux condenser, and thermometer were placed **10** g (**0.034** mole) of octamethylcyclotetrasilazane, **3.8** g (**0.063** mole) of ethylenediamine, and **0.2** g of ammonium chloride. The mixture was stirred at **110°C** for **2.5** hours and **190°C** for one hour. Ammonium chloride, **0.2** g, was added, and stirring was continued at **190°C** for five hours, **200°C** for two hours, and **175°C** at **0.2** mm pressure for two hours. The product was dissolved in xylene, centrifuged, and recovered by distilling the xylene at reduced pressure. The red-brown solid product weighed **8.0** g. Because of incomplete stability in suitable solvents the molecular weight was not determined.

The behavior of this product was different from that of any other that has been prepared. It was quite tough though not particularly hard, and it became resilient on heating in a test tube to **150-200°C**. It became fluid in the temperature range of **200-290°C**, and it bubbled gently while being heated from **300°C** to **440°C**. At **440°C** it boiled rapidly, and the temperature became steady. Boiling for about **15** minutes caused darkening but no rise in temperature, and on cooling to room temperature, the polymer did not exhibit the same physical states that it did on heating. A scum formed on the surface of the resulting dark, sticky polymer after it had stood for several hours at room temperature.

When the reaction product was heated in air at 350-400°C, it became dark and rubbery but did not melt. Subsequent cooling to room temperature produced the toughest rubbery material we have made. The behavior of this polymer may be due to a higher molecular weight than any previously obtained.

n. Octamethylcyclotetrasilazane and ethylenediamine in quinoline, Experiment 2614-63

In a 100-ml, 3-necked flask fitted with a stirrer, reflux condenser, and thermometer were placed 10 g (0.034 mole) of octamethylcyclotetrasilazane, 4.1 g (0.068 mole) of ethylene-diamine, 0.2 g (0.0037 mole) of ammonium chloride, and 40 ml of quinoline that had been purified by distillation from phthalic anhydride and from potassium hydroxide. The mixture was heated at gradually increasing temperatures from 135-323°C for 18 hours. During the first three hours the ethylenediamine refluxed and ammonia was evolved. The quinoline was removed at 139-140°C at 49 mm, leaving a red-brown grease. The product was dissolved in xylene and centrifuged. The xylene was distilled, leaving a red-brown grease. An attempt to estimate the molecular weight by cryoscopy in benzene showed only that it was above 3000.

B. Polymerization With the Aid of a Trifunctional Silane

The reaction of a difunctional silicon halide with a difunctional amine usually led to cyclization in preference to polymerization. However, the amount of polymer produced was increased drastically by mixing a trifunctional and a difunctional silicon halide. When dimethyldichlorosilane was treated with ammonia, only 1% of the product was undistillable. When a 1:9 mixture (by moles) of methyltrichlorosilane and dimethyldichlorosilane was treated with ammonia, 27% of the product was polymeric. When an equimolar mixture of methyltrichlorosilane and dimethyldichlorosilane was treated with ammonia, 90% of the product was polymeric. The details of the work on trifunctional silicon halides were given in Section II. E.

C. Thermal Polymerization of Silazanes

Hexaphenylcyclotrisilazane is known to polymerize when heated in the range of 400-500°C, and use was made of this phenomenon to obtain coatings that did not evaporate while being cured at 500-550°C. The initial results were reported previously.[1] Recently efforts to obtain more information about the structure of the hexaphenylcyclotrisilazane polymer led to a more detailed study of the polymerization in the 400-500°C range. A condensation reaction accounted for part of the observed polymerization approximately according to this equation

$$(Ph_2SiNH)_3 \longrightarrow (Ph\,Si\,N)_x$$
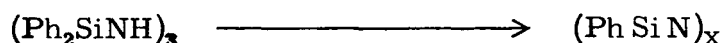
The details of this investigation of the condensation reaction are given below in Section VI. The mixture of methylphenyl silazanes, as described in Section VI, polymerized readily in the 400-500°C range, but pure 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilazane polymerized very slowly at 405°C, which was evidently its boiling point. The silylhydrazine polymer, Section II.A., also polymerized on heating over the entire range from 200-520°C. On the other hand, nonamethylcyclotrisilazane did not polymerize when heated at 400°C in a sealed tube for 456 hours.

At present very little is known about the structural changes that occur among the silazanes and silylhydrazines in the 400-500°C range. It is possible that reactions in this temperature range may be the best means of obtaining high polymers. A patent issued to Groszos and Hall[25] describes the preparation of thermoplastic polymers by heating hexaphenylcyclotrisilazane in nitrogen in sealed tubes at temperatures ranging from 450°C to 700°C. All of their polymeric products were said to soften at 280-300°C. They did not report molecular weights.

The general subject of polymerization of silazanes merits intensive work, because the hydrolytic susceptibility of the thermoplastic polymers that are formed in the 400-500°C range is much less than that of the original silazanes.

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25. S. J. Groszos and J. A. Hall (to American Cyanamic Company) U. S. Patent 2,885,370 (May 5, 1959).

IV. ELASTOMERS

A. Summary

The elastomers that have been produced from silazanes are characterized by exceptional thermal stability and low strength. They are weaker than commercially available elastomers, but they have greater stability at elevated temperatures and greater resilience at low temperatures than any other elastomers that we know to be available. Furthermore, they are highly stable to chemicals and solvents and adhere readily to stainless steel, aluminum, glass, and ceramics. Hence, they probably will be useful as flexible coatings and as impregnating agents for gaskets made of asbestos and fiberglass. Prior to the work reported here, these elastomers had all been made from the reaction product of ethylenediamine with dimethyldichlorosilane.[1] This product, which was termed "ethylenediamine silazane," was heated at 350-400°C in air to form the elastomer. More recently it has been found that some products of the amine-exchange reaction also are converted to elastomers by heating in air at 350-400°C. The products of the amine-exchange reaction that can be converted to elastomers are those that result from the exchange of ethylenediamine with silazanes having two methyl groups attached to each silicon atom. Hence, they are chemically similar to the ethylenediamine silazane.

The strength of the elastomer made from the ethylenediamine silazane was improved by incorporating Santocel colloidal silica as a filler and curing it with a peroxide.

An elastomer was also found in a bottle which contained the distillation residue from a reaction of dimethyldichlorosilane and methylamine. The residue was a viscous liquid when first prepared, but it became a resilient solid on standing in a desiccator for ten months. Chemically the elastomer resembled those made from ethylenediamine silazane.

All of the elastomers that have been made from silazanes resemble silicone rubbers in elemental composition except that they contain from 0.6 to 7% nitrogen, depending on the curing method. In addition, the adhesion and thermal stability of the silazane elastomers distinguish them from the silicone rubbers.

B.   Curing Ethylenediamine Silazane with Peroxide and Filler

1.   Discussion

Elastomers were first produced from ethylenediamine silazane by heating in air at 350-400°C. The product was a dark foamed resilient solid that could easily be crushed with the fingers. Only a small amount of time has been devoted to improvement of the curing method, but there is reason to believe that the strength can be improved without sacrificing thermal stability.

The strength of the elastomer made from ethylenediamine was improved by adding Santocel colloidal silica as a filler and curing with a peroxide. The resulting silazane elastomer could be crushed with the fingers, thereby showing it to be much weaker than either Silastic 80 or Viton A. However, it did not have a foamed structure as did all of the previously examined silazane elastomers, and it could be crushed by hand only with difficulty; this result showed it to be stronger than those made without fillers or peroxides. Neither the silazane elastomers, Silastic 80, nor Viton A, was changed significantly by three days of heating at 260°C; but in 12 hours in air at 350°C Silastic 80 and Viton A lost all of their resilience, while the silazane elastomer still retained much of its elasticity.

2.   Experimental details

The improved silazane elastomer was prepared as follows. A mixture of 10 g of ethylenediamine silazane and 1. 0 g (10% by weight) of Santocel 54 (Monsanto Chemical Company), was stirred until uniform in appearance and heated in an oven at 200°C for five days. In a second experiment, a mixture of 10 g of ethylenediamine silazane, 1 g of Santocel filler, and 0. 3 g of Varox (2, 5-dimethyl-2, 5, di-t-butylperoxyhexane, R. T. Vanderbilt Company) was stirred

until uniform and then heated in an oven at 200°C for five days. At the end of the five-day period at 200°C, both samples were partly solid. The sample without peroxide contained a thick scum of friable material, and the entire sample appeared degraded; but the sample with peroxide contained some soft rubbery material.

The sample containing the peroxide, after standing in air two days was heated again to 150°C for three days. It solidified to an elastic material at the end of this heating period. Further heating of one portion of the solid at 400°C for 15 minutes caused it to foam and lose strength; however, it was still very resilient. A second portion was heated in air at 260°C for 64 hours, and it was apparently unchanged. It was not foamed, and it was stronger than any silazane elastomer previously made as judged by its resistance to crushing between the fingers. When Silastic 80 and Viton A were also heated at 260°C for 64 hours, they were not visibly changed. Consequently, to extend the comparison, all three samples were heated at 350°C in air. In ten hours, Silastic 80 was quite hard, the Viton A was hard but retained a trace of resilience, and the silazane elastomer retained most of its original resilience. At the end of two additional hours of heating (12 hours total) the silazane elastomer still retained most of its resilience and was difficult to crush with the fingers, whereas neither Silastic 80 nor Viton A retained any resilience.

C. Synthesis of Ethylenediamine Silazane by Different Methods

1. Discussion

a. Rochow's method

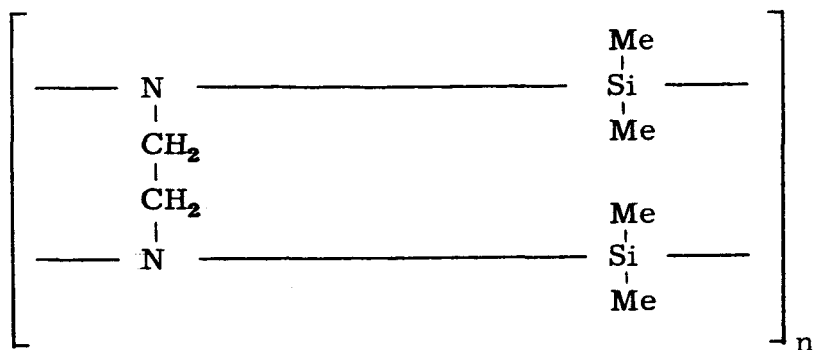In November of 1960 two papers by Minné and Rochow appeared on silazane polymers made from ethylenediamine.[26,27] Their methods of synthesis were different from ours, and consequently it was desirable to determine how their products compared with ours.

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26. R. Minné and E. G. Rochow, J. Am. Chem. Soc. 82, 5625-5628 (1960).

27. R. Minné and E. G. Rochow, J. Am. Chem. Soc. 82, 5628-5630 (1960).

Minne' and Rochow obtained a linear polymer by the reaction of dimethyldichlorosilane with ethylenediamine in xylene. They believed that it had this structure:

$$\left[\begin{array}{c} Me \\ | \\ -Si - NH - CH_2 - CH_2 - NH - \\ | \\ Me \end{array} \right]_n$$
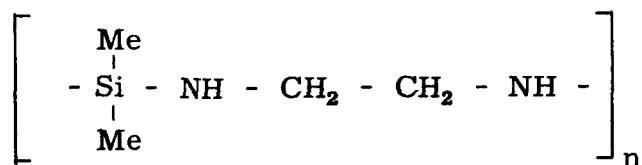
They prepared what they believed to be a ladder polymer from the linear polymer by way of a copper complex and assigned this structure to the ladder polymer:

$$\left[\begin{array}{c} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad Me \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad | \\ ---N----------Si--- \\ \quad | \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad | \\ \quad CH_2 \quad \quad \quad \quad \quad \quad \quad \quad Me \\ \quad | \\ \quad CH_2 \quad \quad \quad \quad \quad \quad \quad \quad Me \\ \quad | \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad | \\ ---N----------Si--- \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad | \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad Me \end{array} \right]_n$$

We repeated their procedures carefully and obtained similar results as far as yields and properties were concerned. However, our analyses differed from theirs as shown in Table XVII. Rochow[26,27] found that his two polymers had essentially the theoretical elemental compositions, but ours differed enough from the theoretical compositions to suggest that we had obtained mixtures.

Table XVII. Comparison of Analyses of Ethylenediamine Silazane Made by
Three Methods

| Element	Method and composition							
	Commercial reagents	Purified reagents Method 1[a]	Purified reagents Method 2[b]	Rochow's linear	Rochow's ladder	Theoretical composition 1 Si:4 N	Theoretical composition 1 Si:2 N	Theoretical composition 1 Si:1 N
Carbon, %	38.94	40.72	40.94	41.32	49.67	40.86	41.33	41.80
Hydrogen, %	9.10	9.47	9.46	9.86	9.35	11.43	10.41	9.36
Nitrogen, %	15.18	19.21	18.53	17.68	11.35	31.78	24.10	16.25
Silicon, %	29.45	26.07	27.14	29.25	21.95	15.93	24.16	32.59
Remainder, % (presumably oxygen)	7.33	4.53	3.93	1.89	7.68	0	0	0
Molecular weight cyclohexane	1900	1200	1100					

[a] Adding dimethyldichlorosilane to ethylenediamine, the "usual" order of addition.
[b] Adding ethylenediamine to dimethyldichlorosilane, the "reverse" order of addition.

[c] Possible structure:
$$H_2N-CH_2-CH_2-NH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-NH-CH_2-CH_2-NH_2.$$

[d] Possible structure:
$$\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-NH-CH_2-CH_2-NH-\right]_x$$

[e] Possible structures:
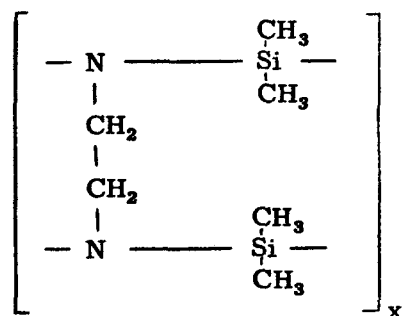
Proposed by Rochow for ladder structure
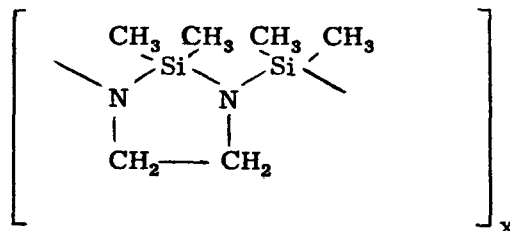
Proposed by us as possible component of all mixtures.

Minné and Rochow assigned the ladder structure to their polymer because of steric factors and their deductions about the type of structure that would normally result from the 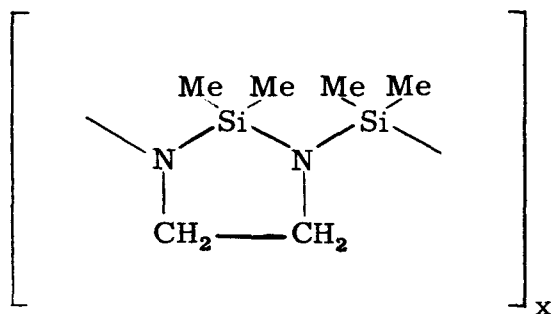copper complex. We believe the following structure should also be considered, at least as a possible component of the original mixture:

$$
\left[
\begin{array}{c}
\text{Me}\quad\text{Me}\quad\text{Me}\quad\text{Me} \\
\diagdown\text{Si}\diagup\quad\diagdown\text{Si}\diagup \\
\diagdown\text{N}\diagup\quad\quad\text{N}\diagup\diagdown \\
| \qquad\qquad | \\
\text{CH}_2 \text{-----} \text{CH}_2
\end{array}
\right]_x
$$

The procedures of Minné and Rochow call for addition of one mole of dimethyldichlorosilane to two moles of ethylenediamine in xylene. In our method one mole of dimethyldichlorosilane is added to five moles of ethylenediamine in benzene. Consequently, it is understandable that there is some difference in the product. They converted the linear polymer to the ladder form by refluxing with cupric chloride in xylene. The samples made by the Rochow method performed similarly to those made by our method. The comparison when all were cured on aluminum panels is shown in Table XVIII. There was less weight loss in our sample, but the coverage, color, flexibility, and adhesion were similar.

Table XVIII. Comparison of Several Ethylenediamine Silazanes
Cured on Aluminum Panels

(Appearance and weight loss in percent compared to weight at 100°C)

Treatment	Rochow's linear	Rochow's ladder	SRI ethylenediamine silazane
1 hr at 100°C			
Color and texture:	lightest yellow-brown smooth	intermediate yellow-brown pebbled	darkest yellow-brown smooth
15 min at 350°C			
Wt. loss, %	30	39	4
Color and texture:	intermediate red-brown smooth	darkest red-brown pebbled	lightest red-brown smooth
2.5 hr at 400°C			
Wt. loss, %	71	70	17

All panels could be bent without cracking the films after 2.5 hr at 400°C. After bending, additional heating at 400°C produced cracks in the linear polymer in 5 min, but the other two were visibly unaffected after 1.5 hr at 400°C.

b. Variations in raw materials and method of addition

In an effort to improve the strength and thermal endurance of the silazane elastomers, several variations in the method of synthesis were tried. The use of carefully purified instead of commercial reagents resulted in a small decrease in the oxygen content as determined by analysis, but the molecular weights were no higher, and no practical advantage of the purification was evident as indicated by the performance of films cured on aluminum panels. The analytical data on the ethylene-diamine silazane made by the different methods are listed in Table XVII.

In another attempt to prepare the ethylenediamine silazane with superior properties, a reaction was carried out in five steps. In the first step an excess of ethylenediamine was allowed to react with dimethyldichlorosilane, and in the second step an excess of the dichlorosilane was added and allowed to react. In this alternating manner, the compound in excess was changed four times, and the reaction was ended with ethylenediamine in excess. The product was essentially the same as the one obtained by all of the other methods, and no advantage of this "series" reaction was evident.

The order of addition of reactants was also reversed in the search for a better method of preparing ethylenediamine silazane. The usual order of addition is to add dimethyldichlorosilane to ethylenediamine. No advantage was found in reversing the order of addition.

2. Experimental details

For comparison, ethylenediamine silazane was prepared according to Rochow's method that produced the linear and ladder polymers.[26,27] The analytical data are in Table XVII.

Ethylenediamine (98%, Union Carbide Chemicals Company) was refluxed four hours with sodium. The mixture was cooled and filtered, and the filtrate was again refluxed with sodium for six hours. After filtering again, the ethylenediamine was distilled over sodium which remained shiny. The dimethyldichlorosilane (Dow Corning Corporation) was distilled, and the fraction boiling at 68-70°C was collected. The amount discarded was approximately 10% of the total, half being higher boiling and half lower boiling than the main fraction.

One of the reactions with the purified reagents was run with the usual order of addition, with the dimethyldichlorosilane being added dropwise to the ethylenediamine dissolved in benzene. A second reaction was run with the reverse order of addition. For the usual order of addition the procedure was as follows: Purified ethylenediamine, 300. 5 g (5. 0 mole), was dissolved in 1500 ml of benzene, and distilled dimethyldichlorosilane, 129 g (1. 0 mole), was added dropwise with stirring over a period of two hours. The mixture was refluxed for four hours; and, after cooling, the two layers were separated in a separatory funnel. The upper layer was freed of benzene by evaporation at reduced pressure. The product, 83 g, was a brown viscous liquid. The molecular weight, as determined cryoscopically in cyclohexane, was 1200.

In the second reaction the quantities and procedure were identical, except that the ethylenediamine was added to the dimethyldichlorosilane, dissolved in benzene. The yield was 87. 7 g of a viscous, colorless, hazy liquid. The molecular weight was 1100.

The elemental compositions of the products from these two reactions are given in Table XVII with the analysis of the product from a reaction with commercial grades of reagents. The molecular weight of the product made from commercial reagents was 1900.

The "series" reaction was conducted as follows: In the first step, dimethyldichlorosilane, 129 g (1. 0 mole), was added dropwise with stirring to a solution of 72. 1 g (1. 2 mole) of ethylenediamine in 1 liter of benzene. The mixture was refluxed for four hours, and the white crystalline mass was filtered off. In the second step, 129 g (1. 0 mole) of dimethyldichlorosilane in 120 ml of benzene was added dropwise with stirring to the filtered solution from the first step. The resulting solution was refluxed for four hours. The rust-colored suspension that formed was not filtered. In the third step, 60. 1 g (1. 0 mole) of ethylenediamine was added, then the mixture was refluxed and filtered as before. The fourth step was the same as the second. In the fifth step, several small additions of ethylene-diamine were made and each was followed by refluxing for two hours, the object being to continue the additions until a slight excess of ethylenediamine persisted. The first addition was 30 g (0. 5 mole); the second was 30 g (0. 5 mole); the last was 15 g (0. 25 mole). The

total dimethyldichlorosilane was 387 g (3.0 moles), and the total ethylenediamine was 208 g (3.45 moles). The resulting mixture was filtered to remove the insoluble salts which were rinsed with benzene. The benzene was distilled off until the pot reached 115°C. At that time, the undistilled solution was cloudy, and so it was clarified by centrifugation. The small amount of volatile matter remaining was not removed, but the amount of it was determined by evaporation of a sample to constant weight in a nitrogen stream. Thus the product was determined to be 171 g of nonvolatile material.

The ethylenediamine silazanes were cured in thin films on aluminum panels to compare their properties. In order to insure the removal of the solvents, comparisons were all based on film weights after heating at 100°C, as shown in Table XVIII. The samples were dissolved in benzene, spread on the weighed panels, and then heated for one hour at 100°C. The weights of samples covering 12 sq cm ranged from 51 to 72 mg. After being weighed, the samples were heated at 350°C for 15 minutes, compared, then heated at 400°C for 2.5 hours, and compared again.

Impregnating filter paper with uncured ethylenediamine silazane and heating the paper produced a flexible sheet of cured silazane with good thermal stability. The treated paper was more stable to heat than the untreated paper, and the product, after heating at a temperature that carbonized the paper, was quite flexible, although it had little strength. After 30 minutes in an oven at 100°C, the impregnated paper was tacky; after 40 minutes at 300°C it was dry, flexible, and tan in color; after 25 minutes at 350°C it was brown and flexible and had much of the original feel of the paper. Other samples having more or less silazane on the paper performed similarly. An untreated paper was charred by 45 minutes at 350°C. After 30 minutes at 400°C a sheet heavily impregnated with silazane was black but quite flexible, and it appeared to be a continuous film.

Small samples of Viton, Silastic 80, and the resilient polymer made from N-methyl silazanes were heated simultaneously to compare their stabilties. All were visibly unaffected by an hour at 250°C. When heated for 30 minutes at 400°C the Viton A blistered and became hard; the Silastic 80 cracked and became hard and brittle; and the resilient polymer made from N-methyl silazanes expanded and cracked on the surface, but it still was resilient.

D. Elastomer Obtained As a By-Product of Nonamethylcyclotrisilazane

1. Discussion

In the preceding year's work, the only elastomers obtained were in the form of thin films or foams. When work was resumed in February, 1961, one of the distillation residues prepared in April, 1960, was found to have congealed to a resilient mass. The residue was obtained in one of the first attempts to synthesize nonamethylcyclotrisilazane by the reaction of dimethyldichlorosilane with methylamine. The amount of residue was only 7.5 g, but its polymerization seemed to be a clue to useful products. Therefore, the elastomer was examined to determine its chemical nature and thermal stability.

When the congealed residue was found after storage for ten months, it was slightly sticky to the touch, and it smelled of methylamine; but an hour of heating at 250°C removed both the stickiness and the odor. By elemental analysis, the congealed residue was found to contain very little nitrogen, as shown in Table XIX. The elemental composition was similar to that of previous samples of ethylenediamine silazane that were cured as thin films. The thermal stability of the congealed residue was similar to that of the cured ethylenediamine silazanes in that it exceeded both Silastic 80 and Viton A in stability at 400°C, and it had more resilience than either of these products at -78°C. It adhered tenaciously to the glass bottle in which it formed. Its strength was considerably less than that of either Silastic 80 or Viton A. No evidence of solubility in organic solvents was found.

In an effort to reproduce the elastomer made from N-methyl silazanes, the distillation residues from two different reactions of dimethyldichlorosilane and methylamine were set aside in four different environments. The environments were at both 115°C and at room temperature in nitrogen and in oxygen. In nine months none of the samples has formed the resilient polymer.

Table XIX.   Elemental Analysis of the Resilient Polymer Made from N-Methyl Silazanes

Element	Found, congealed residue		Cured ethylene-diamine silazane[a]	Cured ethylenediamine silazane[b]	Theoretical for	
	Original	Heated 1 hr at 250°C			C_2H_6SiO[c]	C_3H_9SiN[d]
Carbon, %	32.65	32.38	31.93	31.66	32.39	41.32
Hydrogen, %	8.12	8.16	7.80	8.00	8.16	10.41
Nitrogen, %	1.48	0.55	1.17	0.66	0	32.21
Silicon, %	37.40	37.48	36.00	42.43	37.87	16.06
Remainder, %	20.35	21.43	23.10	17.25	21.58	0

a Cured in a mold by adding successive thin layers of ethylenediamine silazane and curing each at 400°C, for 15 min.

b Cured in air as a thin film on aluminum at 400°C for 30 min; freed by dissolving the aluminum in alkali.
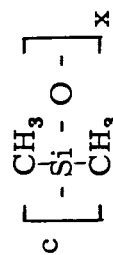
c $\left[\begin{array}{c} CH_3 \\ -Si - O - \\ CH_3 \end{array} \right]_x$ This is approximately the formula for a siloxane rubber.

d $\left[-Si(CH_3)_2NCH_3- \right]_x$
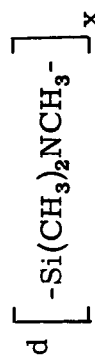
e Determined by the peroxide-fusion method.

2. Experimental details

The resilient polymer made from N-methyl silazanes was originally obtained in the following manner: In a 5-liter, 3-necked flask fitted with a stirrer, thermometer, condenser, and gas inlet tube, were placed 2350 ml of benzene and 250 g (1.94 moles) of dimethyldichlorosilane. Methylamine was passed slowly over the surface of the stirred solution while the temperature was kept below 30°C. Methylamine was passed in slowly to prolong the reaction time. After six hours the mixture was allowed to stand overnight, then the addition of methylamine was resumed for six hours. The mixture was refluxed for three hours. After standing over the weekend, the mixture was filtered, and the clear colorless benzene solution was distilled in a 36 x 1-cm packed fractionating column. At the end of the distillation, the pot temperature was 221°C and the pressure was 0.1 mm. The residue was 7.5 g of a light brown oil, n_D^{25} 1.4355. After standing in a desiccator for ten months, the residue was found to have congealed to a rubbery solid.

The resilient polymer foamed when a large piece of it was heated to determine its stability at 400°C.

The reaction was repeated according to the same procedure. The still residue was placed in storage with nitrogen and oxygen at room temperature and at 115°C. In nine months no polymerization has occurred.

In another effort to reproduce the resilient polymer made from N-methyl silazanes, a preparation of nonamethylcyclotrisilazane was carried out by the method that involves a series of reactions, first with an excess of one reactant and then the other. The reaction was described in detail in Section II. L. 2. The still residue was 19.9 g of a brown viscous liquid that did not distill at 248°C at 0.7 mm. On cooling, some crystals formed in the residue. After one day the liquid portion of the residue was decanted and divided into four parts. Two were placed in vials filled with oxygen, and two were placed in vials filled with nitrogen. One nitrogen and one oxygen vial were placed in a desiccator; and one nitrogen and one oxygen vial were placed in an oven at 115°C. In ten months no polymerization has occurred.

V. STRUCTURAL STUDIES OF POLYMERS FORMED AT HIGH TEMPERATURES

A. Hexaphenylcyclotrisilazane and Methylphenyl Silazanes

1. Discussion

The structure of the polymer made by heating hexaphenylcyclotrisilazane at 500-550°C has been the subject of continuing study throughout the project. Relatively few of the standard structure-proving techniques can be used, because the end product is insoluble except after prolonged boiling in concentrated sulfuric acid, which destroys it. The most direct route to additional information was to study the compounds which are intermediates between hexaphenylcyclotrisilazane and the polymer. Three such intermediates were studied by spectroscopy and elemental analysis. The ease of controlling the experiments suggested that the technique will be useful in the future.

Analyses performed in the past on the polymer made from hexaphenylcyclotrisilazane at 500-550°C indicated that the elemental formula was close to C_6H_5SiN, the molecular weight being unknown. Recent work showed that boiling hexaphenylcyclotrisilazane in a flask caused the elemental formula to progress from $C_{12}H_{11}SiN$ to approximately C_6H_5SiN as the temperature indicated by a thermometer in the melt progressed from 480° to 531°C. This progression is shown graphically in Figure 2, and the data are in Table XX. The temperature that existed in the melt after the reaction reached 531°C was uncertain, because the mass began to solidify, and the thermometer did not indicate the true temperature. In fact it is probable that the thermometer did not indicate the true reaction temperature at any time, because superheating undoubtedly occurred at the walls of the flask. Consequently, a high temperature could exist at the boundary between the melt and the flask, causing the condensation reaction to occur, whereas the thermometer would indicate only the average temperature. The polymer was soluble in benzene until it reached the final solidification point at 531°C. Reaction evidently did not stop at this point, however, because a sample that had been heated at 550°C for 50 minutes had approximately the formula C_5H_5SiN. In the future we hope to refine the experiments by measuring molecular weights, identifying the evolved compounds, studying the chemical properties of the intermediate polymers, and studying the changes that occur above 530°C.
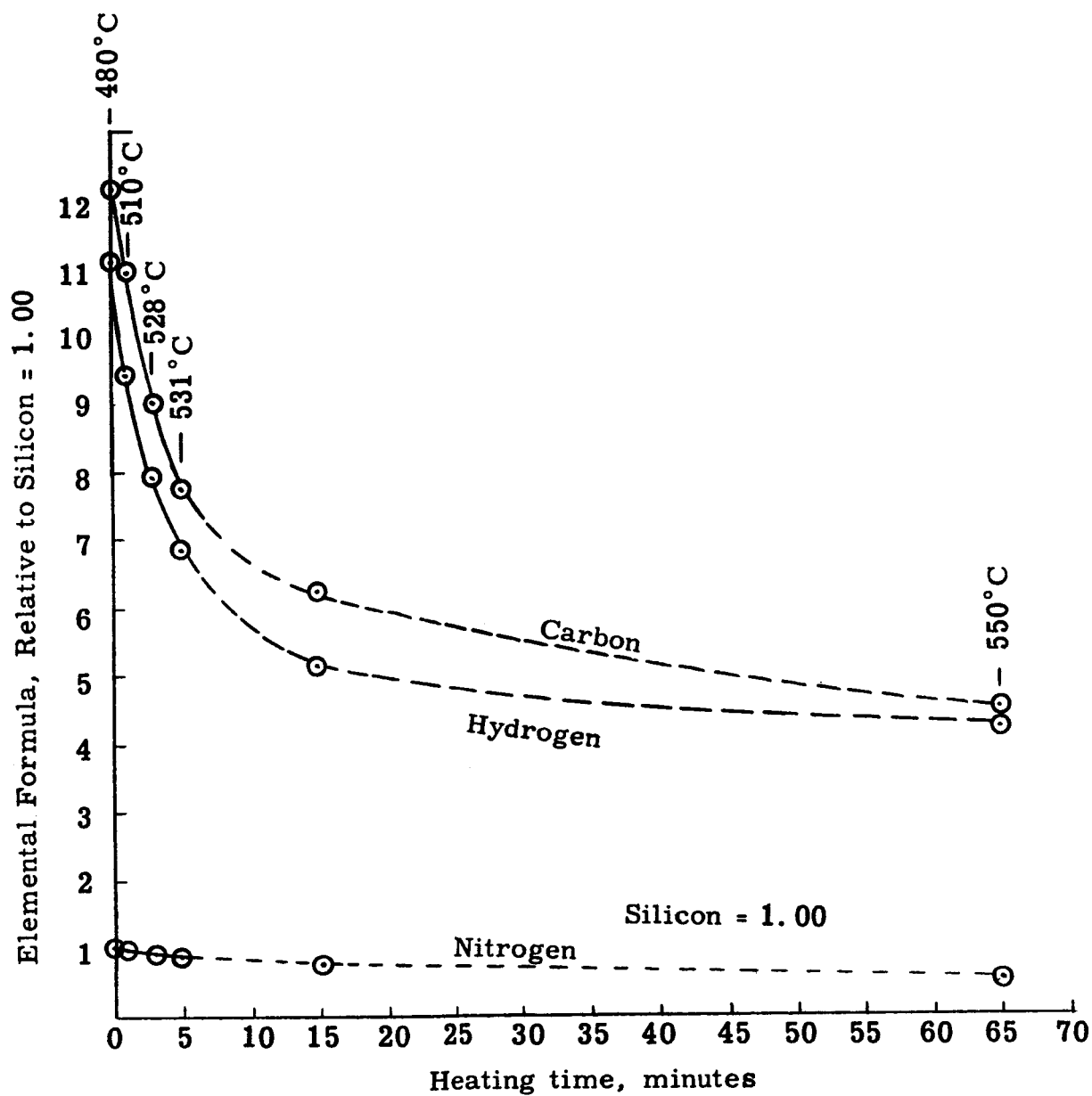
Figure 2. Change in Composition of Hexaphenylcyclotrisilazane Polymers

Table XX. Characteristics of Precursors of the Hexaphenylcyclotrisilazane Polymers

	I	II	III	IV	V	VIa
Time of heating, min	0	1	3	5	15	65
Temperature when sample taken, °C	-	510	528	531	-	550
Approximate m.p. of sample, °C	213-215	197-204	160-163	179-320	infusible	infusible
Physical state, when cool	crystalline	vitreous	vitreous	vitreous	foamed, vitreous	foamed, vitreous
Solubility in benzene	soluble	soluble	soluble	soluble	insoluble	insoluble

Elemental Analyses

	Composition, %	Combining ratio[b]	Composition, %	Combining ratio[b]	Composition, %	Combining ratio[b]	Composition, %	Combining ratio[b]	Composition, %	Combining ratio[b]	Composition, %	Combining ratio[b]
Carbon	73.04	6.08	72.19	6.01	69.30	5.76	65.36	5.44	61.24	5.10	58.83	4.90
Hydrogen	5.58	5.55	5.22	5.19	5.11	5.08	4.84	4.80	4.29	4.25	4.64	4.60
Nitrogen	6.90	0.49	7.29	0.52	7.95	0.57	8.90	0.64	9.41	0.67	8.22	0.58
Silicon	13.97	0.50	15.30	0.55	18.00	0.64	19.70	0.70	23.10	0.82	30.24	1.08
Total	99.49		100.00		100.36		98.80		98.04		101.93	
Ratios to Si = 1												
Carbon		12.16		10.92		9.01		7.77		6.22		4.53
Hydrogen		11.10		9.43		7.94		6.85		5.18		4.25
Nitrogen		0.98		0.95		0.89		0.91		0.82		0.54
Silicon		1.00		1.00		1.00		1.00		1.00		1.00

[a] This sample was polymerized independently. After polymerization it was heated at 550°C for 50 min.

[b] Combining ratio = $\dfrac{\text{composition}}{\text{atomic weight}}$

Infrared spectra suggest that the polymerization of hexaphenyl-cyclotrisilazane is complex. According to the spectra the polymer formed by heating hexaphenylcyclotrisilazane at **500-550°C** apparently contained monosubstituted phenyl rings, but the possibility that disubstituted rings were present is not excluded. Further heating at **700°C** caused some bands to appear that were believed to be the spectra of silicon-hydrogen bonds, and nitrogen-hydrogen bonds were still present. Heating caused a progressive decrease in definition of the bands in the **600** to **1300 cm^{-1}** region, which suggested increasing molecular weight and complexity of structures. The liquid distilled off during the formation of the condensation polymer evidently contained benzene and unidentified silicon-nitrogen compounds.

X-ray diffraction patterns of the polymers made by heating hexaphenylcyclotrisilazane and mixed methylphenylsilazanes are described in Table XXI. Both polymers were prepared by heating at **500-550°C** until the melted reactants became solid.

It is evident that some crystallinity existed in the hexaphenyl-cyclotrisilazane polymers formed at high temperature, but it was weak in comparison to the crystallinity of such polymers as high-density polyethylene. There is no way of knowing, at present, whether the observed crystallinity resides in an impurity or in the main polymer species. However, it can be said with assurance that neither silica, silicon nitride, nor the starting material is responsible. The high d values observed (**11.0** and **12.2**), which are the distances in Angstroms between reflecting planes, indicate that the crystallinity is associated with large molecules.

The following reaction is possibly part of the thermal condensation process:
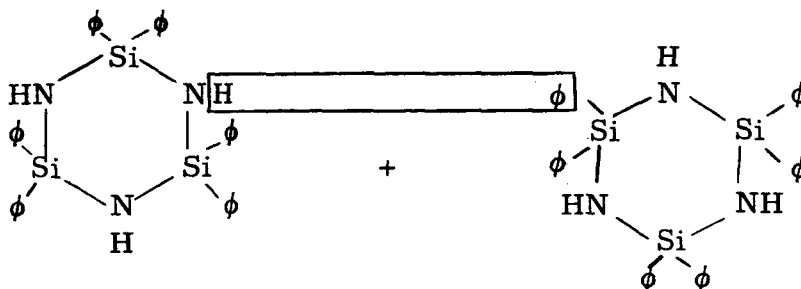
Table XXI. X-Ray Diffraction Patterns of Polymers Made at High Temperature

Hexaphenylcyclotrisilazane				Mixed methylphenyl silazanes				1,3,5-Trimethyl-1,3,5-triphenyl-cyclotrisilazane	
polymer		starting material		polymer		starting material			
d	intensity	d	intensity	d	intensity	d	intensity	d	intensity
12.2	s	9.38	m	11.0	s			10.45	w
		8.27	w					9.48	w
2.02	w	7.59	w	2.00	w			8.30	s
		6.19	m					7.57	w
1.97	m	4.95	s	1.96	m	no pattern		6.14	w
		4.55	m					5.52	w
1.75	w	4.29	w	1.74	w			5.19	w
		4.11	m					4.75	w
1.23	w	3.45	w	1.22	w			4.57	w
		3.29	w					4.37	w
1.15	w	3.16	w	1.13	w			4.13	m
		3.00	w					3.83	w
1.06	w	2.86	w	1.05	w			3.64	w
		2.69	w					3.52	w
		2.55	w					3.33	w
		2.39	w					3.24	w
		2.00	w					3.11	w
		1.96	w					3.06	w
		1.90	w					2.87	w
								2.76	w
								2.63	w
								2.57	w
								2.04	w
								2.00	m
								1.77	w
								1.25	w
								1.16	w
								1.08	w

s = strong
m = medium
w = weak

After polymerization has progressed far enough to immobilize the molecules and restrict the simple elimination of benzene between Si-ϕ and N-H groups, the fragmentation of benzene may occur, permitting the formation of SiH bonds from the fragments.

2. Experimental details

A series of five samples was prepared to study the progressive polymerization of hexaphenylcyclotrisilazane.

Hexaphenylcyclotrisilazane, 5 g, that had been recrystallized from benzene was placed in a test tube with a side arm attached. The starting material was Sample 1. A 600°C thermometer was placed loosely in the test tube, and the apparatus was flushed with nitrogen. Thereafter nitrogen was passed slowly into the side arm to maintain an inert atmosphere in the tube. The tube was heated gently with a gas flame. The crystals melted at about 215°C. Continued heating produced a few bubbles, but the liquid did not appear to boil until the melt reached 480°C. Boiling was resumed while the melt temperature rose to 510°C in one minute. At this time heating was discontinued while Sample II was removed with a small stainless-steel scoop. Heating was resumed, and after two additional minutes of boiling with the temperature at 528°C, Sample III was taken. After two additional minutes of boiling, Sample IV was taken at 531°C. As the sampling scoop was withdrawn, the melt formed fibers, indicating high molecular weight. Shortly after Sample IV was taken, a solid began to appear in the melt; and thereafter the temperature measurement was erratic because of poor contact between the walls of the tube, the reaction mixture, and the thermometer. Heating and stirring were continued until the entire mass became solid. The product was Sample V. For the purpose of plotting Figure 2, the time to reach complete solidification was estimated to be ten minutes. However, none of the time-temperature data taken after solid began to form should be regarded as accurate. The questionable data appear as dotted lines in Figure 2. Sample VI was prepared independently of the other five by heating the polymerized solid in an oven at 550°C for 50 minutes. Then it was extracted with acetone in a Soxhlet extractor.

The preparation of the mixture of methylphenyl silazanes was described in detail in the report of the preceding work.[1] Methylphenyl-dichlorosilane dissolved in benzene was treated with ammonia. When the absorption of ammonia was complete, the mixture was refluxed, the ammonium chloride was filtered off, and the benzene was removed by distillation. The product was a partially crystalline paste that was termed the mixture of methylphenyl silazanes. From this paste, a small amount of 1, 3, 5-trimethyl-1, 3, 5-triphenylcyclotrisilazane was separated by recrystallization.
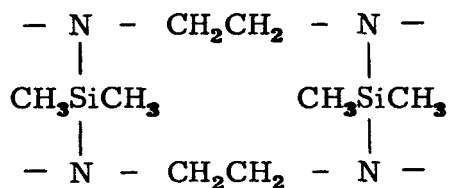
This compound did not readily undergo polymerization by heating. Instead it boiled at approximately 405°C and was stable even on prolonged refluxing. However, the mixture of methylphenyl silazanes had a high enough boiling point for the polymerization temperature to be reached easily. The mixture of methylphenyl silazanes was heated in an open test tube until the melt temperature reached 520°C. At this point the product was soluble in benzene. It performed well as a coating material, as described below in Section VI. Further heating caused solidification. The x-ray diffraction data on the resulting foamed vitreous solid are reported in Table XXI.

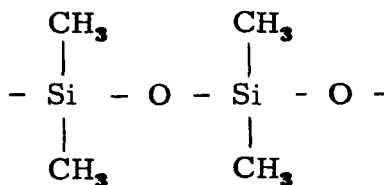## B. Elastomer Made from Ethylenediamine Silazane

1. Discussion

Infrared spectra of cured and uncured ethylenediamine silazanes suggested that very little N-H was present either before or after curing. This observation is compatible with a structure in which all four available hydrogen atoms in ethylenediamine have been replaced by silicon atoms. Infrared spectra revealed surprisingly few differences between the cured and uncured ethylenediamine silazanes. Accordingly, infrared data did not help define the structure of the cured polymer.

Ethylenediamine silazane films cured on aluminum and then set free by dissolving the aluminum in alkali had the elemental analysis reported in Table XXII, Column C. A sample made by curing ethylene-diamine silazane in successive layers in a mold had a similar elemental composition (Table XXII, Column B), and both were close to the theoretical values for a siloxane rubber (Table XXII, Column F). The similarity of the cured ethylenediamine silazanes to siloxane rubber prompts a search for an explanation of the greater thermal stability and better adhesion of the ethylenediamine silazanes. It is possible that the superior adhesion of the silazanes results from attachment to the substrate through the nitrogen atoms or the NH groups prior to curing. Curing subsequently eliminates most of the nitrogen but does not destroy adhesion. It is also possible that steric factors influence the properties of the cured silazane elastomers. Minné and Rochow[26,27] believed their polymer made from ethylenediamine and dimethyldichlorosilane had a "ladder" structure:

$$
\begin{array}{ccc}
-\text{N} - & \text{CH}_2\text{CH}_2 & - \text{N} - \\
| & & | \\
\text{CH}_3\text{SiCH}_3 & & \text{CH}_3\text{SiCH}_3 \\
| & & | \\
-\text{N} - & \text{CH}_2\text{CH}_2 & - \text{N} -
\end{array}
$$

This structure is compatible with the infrared data showing that few NH groups were present. It is likely that curing of the ladder structure would lead to a product that would be different in spatial arrangement from the siloxane rubbers, which originate from this structure

$$
\begin{array}{ccc}
\text{CH}_3 & & \text{CH}_3 \\
| & & | \\
-\text{Si} - \text{O} - & \text{Si} & - \text{O} - \\
| & & | \\
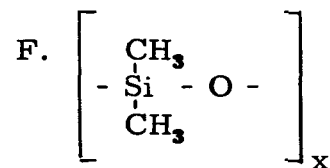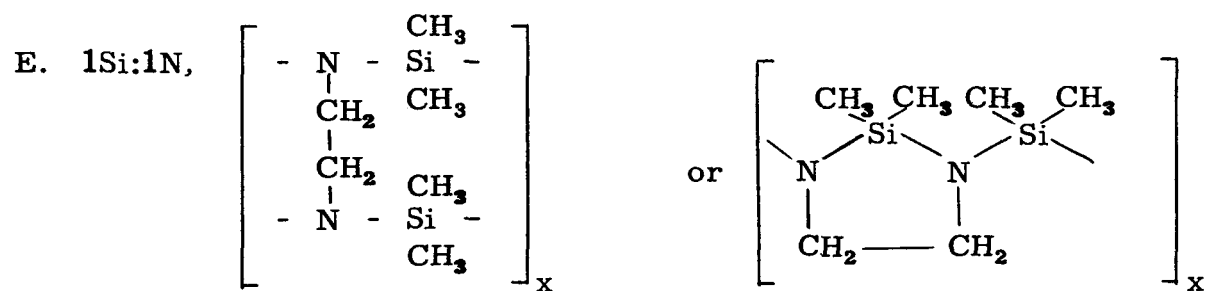\text{CH}_3 & & \text{CH}_3
\end{array}
$$

by the formation of cross-links in about one of each hundred of the repeating methyl units.

Table XXII. Elemental Analysis of Resilient Polymer Made from
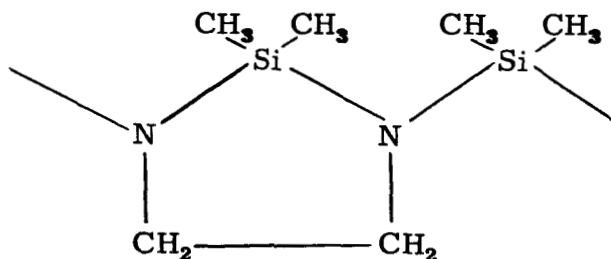Ethylenediamine Silazane

| | Found for ethylenediamine silazanes | | | Theoretical for | | |
| | Uncured | Cured | | | | |
Element	A	B	C	D	E	F
Carbon, %	40.72	31.93	31.66	41.33	41.80	32.39
Hydrogen, %	9.47	7.80	8.00	10.41	9.36	8.16
Nitrogen, %	19.21	1.17	0.66	24.10	16.25	0
Silicon, %	26.07	36.00	42.43	24.16	32.59	37.87
Remainder, %	4.53	23.10	17.25	-	-	21.58

A. Reaction product of dimethyldichlorosilane and methylamine, Table XVII, Method 1.

B. Cured in a mold by adding successive layers of ethylenediamine silazane and curing each at 400°C for 15 min.

C. Cured in air as a thin film on aluminum at 400°C for 30 min, freed by dissolving the aluminum in alkali, then extracted with acetone in a Soxhlet extractor.

D. 1Si:2N, $-Si(CH_3)_2-NH-CH_2-CH_2-NH-$

E. 1Si:1N,

$$\left[\begin{array}{c} \quad\quad CH_3 \\ -N - Si - \\ \;|\quad\quad | \\ CH_2\quad CH_3 \\ \;| \\ CH_2\quad CH_3 \\ \;|\quad\quad | \\ -N - Si - \\ \quad\quad CH_3 \end{array} \right]_x$$

or

$$\left[\begin{array}{c} CH_3\;\;CH_3\;\;CH_3\;\;CH_3 \\ \;\;\diagdown\;/Si\diagdown\quad\;/Si\diagdown \\ N\quad\quad N \\ |\quad\quad | \\ CH_2 ——— CH_2 \end{array} \right]_x$$

F.

$$\left[\begin{array}{c} CH_3 \\ -Si - O - \\ \;|\; \\ CH_3 \end{array} \right]_x$$

This is approximately the formula of a siloxane rubber.

As mentioned previously, Minné and Rochow assigned the ladder structure to their polymer because of steric factors, including the type of structure that they believed would result from the copper complex. Inasmuch as none of our ethylenediamine silazanes clearly fit any single proposed structure, we suspect there may be several involved in our products. In addition to Rochow's ladder and linear structures five-membered rings may be present, as mentioned above.

This structure also agrees with the infrared suggestion that few -NH groups were present.

2. Experimental details

The acetone-extracted film mentioned in Table XXIII was prepared by curing an ethylenediamine silazane film in air at 350°C on aluminum foil. The foil was then dissolved in 8% aqueous sodium hydroxide solution. The freed film was extracted for 1.5 hours in a Soxhlet extractor with acetone. The film lost only 2% by weight. A similar film was freed by dissolving the aluminum in 10% hydrochloric acid. The infrared spectrum and appearance of the film set free with acid were the same as the spectrum and appearance of the film set free with alkali. The infrared spectra were obtained on pulverized samples incorporated into potassium bromide discs.

VI. PROTECTIVE AND INSULATING COATINGS

The initial work on coatings was reported previously[1] and is summarized briefly here. Silazanes that could be heated to the polymerization temperature without evaporating could be applied to aluminum and steel to form protective coatings that were electrical insulators. Films made from ethylenediamine silazane were highly flexible, but they were red-brown and easily scratched and had the least thermal endurance. Films made from partially polymerized hexaphenylcyclotrisilazane were hard, brittle, and colorless and had the greatest thermal endurance. One of the best combinations of properties was obtained with a 50-50 mixture of ethylenediamine silazane and partially polymerized hexaphenylcyclotrisilazane. This film when cured on aluminum foil was tough, and it could be creased between the fingers without cracking. It endured 450°C in air for 30 minutes without apparent degradation. It has now become routine to check the coating properties of each new silicon-nitrogen compound produced.

In previous work, silazane coatings were not successfully applied to copper, because the copper oxidized while the coating was being cured. Several different silazanes were tried with curing in nitrogen, and the one that performed the best was the partially polymerized mixture of methylphenyl silazanes which was described in the report of the preceding year's work.[1]

Methylphenyldichlorosilane was treated with ammonia in benzene solution until no further reaction was detectable. The ammonium chloride was filtered off, and the benzene was distilled at reduced pressure. The undistilled product was boiled in an open test tube until the temperature of the melt reached 520°C. Longer heating at 520-550°C would have converted the melt to a solid. The melt cooled to a pale yellow glassy solid that was soluble in benzene. The glassy solid, 0.2 ml of a 10% solution in benzene, was placed on a copper panel and spread evenly over an area of 12 sq cm. The film was dried under an inverted funnel through which a stream of nitrogen was passing. The film, in the nitrogen atmosphere, was then heated for five minutes on a hot plate at 220°C and finally for 20 minutes at 550°C. The coated sheet could be bent over a mandrel with 4-mm radius without cracking. Subsequent heating in air at 550°C for 15-30 minutes caused oxidation of the copper except where it was coated. A sample of film was intact after nine hours in air at 275°C, but it would not stand bending after that treatment.

Coatings were applied to aluminum wire in the following manner: A mixture containing 70% ethylenediamine silazane and 30% hexaphenyl-cyclotrisilazane (partially polymerized by heating) was dissolved in benzene so that the silazane concentration was 45%. An aluminum wire was cleaned with sodium hydroxide solution, rinsed with water, and then dipped into the silazane solution. The coating was cured ten minutes at 250°C, and then it was dipped and cured once more at 250°C. The coating was cured at 400°C for 15 minutes and at 450°C for 15 minutes. The cured coating successfully resisted the passage of current when about two inches of wire was dipped in salt solution, as tested with a Triplett Ohmmeter at 22 volts. Hence, the resistance was greater than one megohm. The coatings suffered a very small amount of mechanical damage when the wire was doubled and the two parts were twisted tightly together by hand.
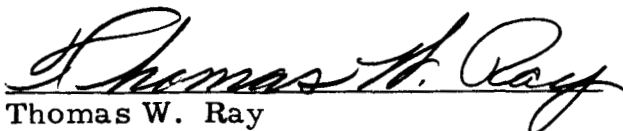
VII. LUBRICATING PROPERTIES

It was desirable to know whether silazanes are promising as lubricants. Accordingly two samples were prepared and submitted to the George C. Marshall Space Flight Center for evaluation.
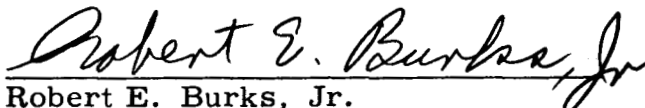
The first sample was 400 g of hexamethylcyclotrisilazane. The second was a 50-50 blend of nonamethylcyclotrisilazane and the polymer (Section II. E.) made by the reaction of ammonia with a mixture of dimethyldichlorosilane and methyltrichlorosilane. The two materials were mixed and heated until the melt temperature rose to 280°C. On cooling the mixture was a heavy grease at 125°C and remained so when it reached room temperature. Neither of the two samples was judged to have interesting lubricating properties.
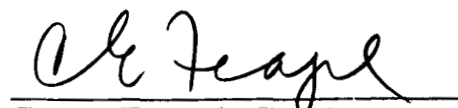
ACKNOWLEDGMENTS

The assistance, comments, and advice of Mr. James E. Curry of the George C. Marshall Space Flight Center are greatly appreciated. The assistance of Mr. Robert E. Lacey, Senior Chemical Engineer, who helped plan and interpret the research, is also appreciated. Mr. William L. Mayfield, Research Technician, and Mrs. Jeanette E. Marstrander, Associate Chemist, assisted with the laboratory work.

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